

Behavior of alkali feldspars: Crystallographic properties and characterization of composition and Al-Si distribution

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ABSTRACT

Four new alkali feldspar ion-exchange series have been synthesized, three with topochemically monoclinic Al-Si distributions ranging from sanidine to relatively ordered orthoclase, the other a microcline–low albite series. Parent materials for three series have previously been studied by single-crystal techniques, so Al-Si distributions are well characterized. Unit-cell dimensions and volumes have been measured for all series members and, with data for a previously reported fifth series, have been analyzed as a function of both composition and Al-Si distribution.

The *a* unit-cell dimension, commonly used as a measure of composition in alkali feldspars, is affected to a small but significant extent by Al-Si distribution and also apparently does not vary linearly with composition, as has previously been assumed. Variation of the *b* and *c* unit-cell dimensions with composition is best analyzed separately for triclinic and monoclinic parts of the topochemically monoclinic series. Furthermore, *b* is not a linear function of *c*, an assumption that until now has been made in using these dimensions to calculate Al-Si distributions in alkali feldspars.

Variation of *c* with mole fraction $KAlSi_3O_8$ (N_{Or}) is linear in both the triclinic and the monoclinic parts of the topochemically monoclinic alkali feldspar series, as well as in the potassic region of the low albite–microcline series. In addition, $\Delta c/\Delta N_{Or}$ slopes are virtually constant for all series. This provides an ordering parameter, c_K , which for alkali feldspars with $N_{Or} > 0.32$ (feldspars with $N_{Or} < 0.32$ require other equations given in the text) may be computed from the observed *c* value of an alkali feldspar (c_{obs}) and its composition as $c_K = c_{obs} + 0.038(1 - N_{Or})$. For natural feldspars, c_K varies from about 7.180 Å for high sanidine to approximately 7.222 Å for maximum microcline.

The distribution of Al and Si between the T_1 and T_2 tetrahedral sites of an alkali feldspar (measured by the ordering parameter *Z*, where *Z* varies from 1.0 for a perfectly ordered feldspar to lower values with disordering) may be calculated from c_K as $Z = -138.575 + 19.3153 c_K$. Mole fractions of Al in T_1 and T_2 are given by $N_{Al(T_1)} = -34.3939 + 4.82884 c_K$ and $N_{Al(T_2)} = 34.8939 - 4.82884 c_K$. These equations are valid for both topochemically monoclinic and triclinic feldspars and improve the precision with which Al-Si distributions can be calculated.

INTRODUCTION

Until the present time three types of alkali feldspar series have been studied—ion-exchange series, short-term crystallization series, and long-term crystallization series (Hovis, 1980). The short-term crystallization series (Donnay and Donnay, 1952; Orville, 1967; Luth and Querol-Süné, 1970) have highly disordered Al-Si distributions. Even the long-term crystallization series (Kroll, 1971; Kroll et al., 1980) are relatively disordered, owing to the extremely long annealing times required to achieve Al-Si redistribution at temperatures below 750°C. Only in ion-exchange series have relatively ordered alkali feldspars been investigated. Most of the work on these has been done on highly ordered, topochemically triclinic feldspars (microcline–low albite series of Orville, 1967; Waldbaum and Robie, 1971; and Kroll in Kroll and Ribbe, 1983;

also see Hovis and Peckins, 1978). Only one intermediate series, based on a specimen of orthoclase (Wright and Stewart, 1968), has been investigated until now.

Currently, information is lacking on topochemically monoclinic alkali feldspar series with Al-Si distributions more ordered than those of the orthoclase series mentioned above. Furthermore, no series has been synthesized with an Al-Si distribution possibly corresponding to that in alkali feldspar from a hydrothermal vein deposit, such as the well-known Alpine “adularias,” nor are there any series between orthoclase and the highly disordered sanidine-analbite series, e.g., feldspars with Al-Si distributions from certain igneous environments.

Most research on alkali feldspar series has dwelt on unit-cell dimensions and various relations among interaxial angles. Thermodynamic data on these series are even more

Table 1. Chemical analysis for Madagascar orthoclase, USNM B18938 (by electron microprobe, D. Appleman)

Oxide	Weight percent	Element	Cations per 8 oxygens
SiO ₂	64.06	Si	3.015
Al ₂ O ₃	17.42	Al	0.966
FeO	0.50	Fe	0.020
MgO	n.d.*	Mg	n.d.
CaO	n.d.	Ca	n.d.
BaO**	n.d.	Ba	n.d.
K ₂ O	15.74	K	0.945
Na ₂ O	0.65	Na	0.059

*n.d. = not detected
**BaO analysis by atomic absorption spectroscopy

limited. Apart from molar volumes, thermodynamic data are available on one very disordered topochemically monoclinic series (Hovis and Waldbaum, 1977; Hovis, 1979b) and one ordered topochemically triclinic series (Waldbaum and Robie, 1971).

It is the purpose of this paper to report on the synthesis and study of four new alkali feldspar series. Three series have Al-Si distributions between those of microcline and sanidine, and the fourth is a new low albite-microcline series. Structural refinements done previously by single-crystal X-ray diffraction and neutron diffraction techniques on parent materials used to synthesize three of the series allow precise characterization of the Al-Si distributions of these series.

Explanations of *why* the unit-cell dimensions of alkali feldspars vary the way they do have been made by Stewart and Ribbe (1969), as well as others mentioned in Smith (1974) and Kroll and Ribbe (1983). The emphases of this paper are to fill in the gaps in cell-parameter data, to analyze a large amount of crystallographic data based on an internally consistent set of chemical analyses, and to discuss how best to calculate Al-Si distributions in alkali feldspars using lattice-parameter data.

In addition to this investigation, solution calorimetric experiments have been conducted on three of the series to determine enthalpies of K-Na mixing and their relationship to Al-Si distribution. This part of the investigation, as well as volume data, will be discussed in a separate paper (Hovis, in prep.).

DESCRIPTIONS OF PARENT FELDSPARS

In order to produce an alkali feldspar ion-exchange series, one starts with a parent material and makes other feldspars by having the parent material exchange K and Na ions with another K- or Na-bearing substance. In the past, aqueous K-Na chloride solutions have been used as an exchange medium (e.g., Orville, 1963), as have various K-Na halide molten salts (e.g., Waldbaum, 1966). Because ion-exchange rates are fast and experimental temperatures are low relative to those conditions required for Al-Si redistribution, the newly made feldspars will have the same, or very nearly the same, Al-Si distribution (see Hovis, 1980) as the parent material. The four alkali feldspar series studied here were based on samples of St. Gotthard adularia no. 7007, Madagascar orthoclase no. B18938, Eifel sanidine no. 7002, and Amelia low

albite no. 7010. Except for the orthoclase, these parent materials have been described previously (Hovis, 1974; Waldbaum, 1966; Waldbaum and Robie, 1971). New chemical data for the adularia, sanidine, and albite are given in Table 3.¹ The orthoclase specimen, obtained from the Smithsonian Institution (where part of the specimen remains) was originally a single crystal 2.4 cm on a side, light yellow, transparent (gemmy), and nonperthitic as determined by both microscopic and X-ray examination. Atomic absorption analysis by Suhr indicates the mole fraction of KAlSi₃O₈ (*N_{Or}*) to be 0.9343. The specimen also has been analyzed by electron microprobe (Table 1, Appleman, personal comm.), which yielded an *N_{Or}* value of 0.9409. Orthoclases from Madagascar are well known for their iron content; however, Appleman's analysis shows this specimen to have a calculated KFeSi₃O₈ content of only 2.0 mol%.

Structures of the adularia, sanidine, and low albite have been refined using single crystal X-ray and neutron diffraction techniques. Tetrahedral site occupancies have been calculated from the data and are given in Table 13 and discussed later in the paper.

SYNTHESIS TECHNIQUES

Two techniques were employed to synthesize feldspars of various K/(K + Na) ratios. In the first, parent feldspars were ground to -325 or -400 mesh size and elutriated. For potassic parent materials, a portion of each powder was placed with a large excess of Na-rich chloride in a Pt crucible and heated to ~815°C for up to 40 h. At this temperature, ion exchange took place between the molten salt and feldspar, resulting in a Na-rich equivalent of the feldspar. After cooling, the feldspars were separated from the solid chloride by dissolving the chloride in water. Several rinses assured that all of the chloride was removed. A similar procedure was followed for the low albite, except that ion exchange was conducted in molten KCl.

Initial intermediate compositions were created by mixing the ion-exchanged feldspar powder with the natural feldspar powder in various proportions to achieve different compositions. A few additional intermediate compositions were achieved by combining various feldspars of intermediate compositions. Mixed powders were compressed in a cylindrical Pt crucible and annealed at ~930°C. Under these conditions, K and Na ions exchanged between grains of the two feldspars. The powders were removed from the furnace every 24 h and remixed in acetone, optimizing the chances for complete homogenization. Relatively homogeneous feldspars were produced in ~120 h, but some required longer heating.

The second technique used to create feldspars of intermediate K/(K + Na) ratios was to ion-exchange feldspar powders in a mixed (Na,K)Cl molten salt. In this way the parent feldspar exchanged to an intermediate composition. It was thought that this technique might produce better homogeneity in the feldspars than the homogenization of mixed powders. Two problems arose with this synthesis technique. First, exchange was not normally complete after the initial run, and in a number of instances, achievement of the desired composition required several runs. Second, even after the final exchange, the resulting feldspar was generally not of satisfactory homogeneity, which necessitated further annealing similar to the homogenization of feldspar powders mentioned above.

¹ To receive copies of Tables 2 and 3, order Document AM-86-308 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006. Please remit \$5.00 in advance for the microfiche.

Detailed synthesis histories of all feldspars studied during this investigation are given in Table 2 (see footnote 1).

STATES OF THE RESULTING FELDSPARS

Chemical composition

Most of the ion-exchanged feldspars were analyzed (using atomic absorption spectroscopy) for Na_2O and K_2O by Norman Suhr of Pennsylvania State University (Table 3; see footnote 1). It has been shown previously (Waldbaum, 1966; Hovis, 1971) that the exchange of Na and K ions in alkali feldspars does not affect the levels of divalent or trivalent ions in the feldspars. Spot checks on Ba levels in various members of the adularia and Eifel sanidine series, as well as more recent checks for Fe, Mg, Ca, Ba, and Sr on some ion-exchanged plagioclases, confirm this (Hovis, unpub. data).

More complete chemical analyses of solid-solution impurities in the parent feldspars for the adularia and sanidine series can be found in Phillips and Ribbe (1973, p. 264) and in Hovis (1974, p. 118). The former authors did not analyze for Ba, but the present work shows that some Ba exists in both feldspars (Table 3). Complete chemical data on Amelia low albite are given in Waldbaum and Robie (1971).

Homogeneity

The synthesis techniques used here can lead to Na-K inhomogeneity in the samples. Therefore, feldspars were routinely checked for homogeneity by inspection of the X-ray pattern of each feldspar to see if broadened peaks, particularly the composition-sensitive (201) peak, could be found. Whenever broadened peaks were observed, the feldspar was returned to the furnace for additional annealing.

To further check for homogeneity, 8 to 11 points on three specimens each from the adularia and orthoclase series were analyzed by microprobe. The average analyses and their standard deviations are given in Table 4. Although such small numbers of data points are not statistically valid for the purpose of determining the compositions of the feldspars, the standard deviations do indicate that the compositional ranges within the grains are small. For reasons explained previously (Hovis and Waldbaum, 1977, p. 683) these levels of inhomogeneity have little effect on the thermodynamic mixing properties to be reported later (Hovis, in prep.).

Check on Al-Si distribution

Since it is our aim to deal with series whose members are of a single structural state, it is important to check the state of Al-Si order in the various feldspar series. It has been established that the temperatures (800–825°C) and relatively short times (24 h) of molten-salt ion-exchange runs do not detectably change the Al-Si distribution of an alkali feldspar (Waldbaum, 1966; Waldbaum and Robie, 1971; Hovis, 1977). It also has been noted (Hovis, 1979a, 1980) that even the higher temperatures (900–935°C) and longer times (generally 120 h) of the dry homogenizations do not seem to affect Al-Si distributions. In the current study, however, some of the homogenization times were longer than those used previously. This was true of all intermediate members of the microcline series, which homogenized more slowly than members of other series and thus were left in the furnace for about 240 h. Note that there are two feldspars of this series (nos. 8207 and 8429) at essentially the same composition but with different homogenization times (316 and 252 h, respectively). The reason for this will be discussed in greater detail below. Homogenization times also were longer for certain members of

Table 4. Compositions of feldspars from intermediate members of two alkali feldspar series, based on electron-microprobe analyses

Adularia series members	N_{Or}	N_{Ab}
7917	0.261 ± .021	0.738 ± .021
7914	0.512 ± .038	0.488 ± .038
7918	0.707 ± .029	0.293 ± .029
Orthoclase series members		
7815	0.299 ± .040	0.701 ± .040
7905	0.467 ± .021	0.533 ± .021
7908	0.703 ± .004	0.297 ± .004

other series, for example, no. 7927 of the adularia series (189 h total), no. 7906 of the orthoclase series (240 h for the part of the sample having the most complex history), and no. 8201 of the Eifel sanidine series (250 h).

To check the Al-Si distributions, at least two members of each series were back-exchanged in molten KCl to produce a potassic feldspar whose unit-cell dimensions could be compared with those of the K-exchanged equivalent of the parent feldspar. Because sodic feldspars generally disorder more readily at a given temperature than do potassic feldspars, the members of the various series chosen for these experiments were either the most sodic intermediate members of the series, or the most sodic intermediate members having had the longest homogenization times. All members of the microcline series were checked because of the longer homogenization times. Unit-cell dimensions for the resulting feldspars are given in Table 5 and may be compared with data for the appropriate potassic feldspars of Table 6.

Members of the high sanidine series have Al-Si distributions which were based on a higher disordering temperature than that of the homogenization. Since reordering is known to be extremely sluggish under dry conditions, the high sanidine series was not included in this analysis.

Comparison of the unit-cell dimensions of feldspars listed in Table 5 with those of their K-rich equivalents in Table 6 reveals little evidence for disordering during the homogenizations of intermediate members of topochemically monoclinic series. If disordering had occurred, feldspars of Table 5 would have significantly larger *b* dimensions and smaller *c* dimensions than the comparable feldspars of Table 6. Values of *b* for feldspars of Table 5 are larger in only three of eight cases. Although values of *c* are smaller in six of the eight cases, differences for K-exchanged natural versus homogenized feldspars are in the worst cases only about twice the combined uncertainties of the refined values.

A similar analysis of the data for topochemically triclinic feldspars reveals that a small degree of disordering may have taken place at intermediate and sodic compositions, indicated by the larger *b* and smaller *c* dimensions of K-exchanged feldspars no. 8414, 8410 (and 8418), and 8415 (synthesized from feldspars no. 8047, 8207, and 8205, respectively) relative to no. 71104. The effect is especially pronounced in intermediate feldspar no. 8207, which homogenized slowly apparently because of the close proximity of its composition to the critical composition of the microcline-low albite solvus and because of the high critical temperature of the solvus for these feldspars (Bachinski and Müller, 1971; also Hovis, 1983 and in prep.), probably not much below the temperature of the homogenization. This necessitated a homogenization time of 316.0 h. A second series member, no. 8429, was synthesized at the same composition using finer-grained powders as starting materials (−400 mesh instead of −325 mesh,

Table 5. Lattice parameters for K-exchanged intermediate members of various ion-exchange series

Potassic feldspar and refinement feldspar	Parent feldspar	a(Å)	b(Å)	c(Å)	α (deg)	β (deg)	γ (deg)	$V(\text{Å}^3)$	Scans, lines
Eifel Sanidine Series									
8419	8201	8.6005 (12)	13.0191 (17)	7.1841 (11)	90.0	115.997 (11)	90.0	723.02 (13)	2, 54
L0478M 72015 L0376M	72001B	8.6025 (8)	13.0262 (10)	7.1871 (6)	90.0	115.989 (6)	90.0	723.94 (7)	2, 51
Orthoclase Series									
7916	7735	8.6012 (8)	12.9938 (9)	7.1994 (7)	90.0	116.052 (6)	90.0	722.87 (7)	3, 90
L0371M 7915 L0370M	7906	8.6053 (8)	12.9964 (9)	7.2016 (6)	90.0	116.054 (6)	90.0	723.56 (7)	3, 101
Adularia Series									
7928	7927	8.5995 (9)	12.9689 (14)	7.2134 (9)	90.0	116.054 (7)	90.0	722.72 (9)	3, 92
L0304M 73023 L0379M	73011E	8.5932 (9)	12.9686 (14)	7.2091 (9)	90.0	116.029 (8)	90.0	721.91 (10)	4, 73
73025 L0378M 7204 L0377M	73013E 7196C	8.5955 (15)	12.9719 (25)	7.2064 (13)	90.0	116.048 (12)	90.0	721.90 (16)	3, 61
7204 L0377M	7196C	8.5972 (10)	12.9688 (16)	7.2123 (9)	90.0	116.030 (9)	90.0	722.57 (11)	2, 45
Microcline Series									
8415	8205	8.5862 (10)	12.9658 (19)	7.2180 (12)	90.577 (13)	115.932 (11)	87.811 (14)	722.10 (13)	4, 67
L0464T 8410 L0460T	8207	8.5896 (12)	12.9691 (30)	7.2122 (14)	90.509 (16)	115.967 (12)	87.981 (19)	721.85 (17)	4, 62
8418 L0468T 8430	8207	8.5893 (8)	12.9687 (17)	7.2103 (10)	90.545 (11)	115.953 (8)	87.983 (11)	721.71 (11)	4, 64
L0510T 8414 L0462T	8429	8.5884 (7)	12.9678 (12)	7.2164 (11)	90.598 (8)	115.958 (8)	87.784 (8)	722.07 (10)	4, 76
8416 L0466T 8417 L0467T	8047	8.5875 (9)	12.9676 (17)	7.2168 (10)	90.570 (11)	115.936 (9)	87.840 (11)	722.18 (11)	4, 66
	8204	8.5865 (10)	12.9591 (19)	7.2173 (11)	90.597 (12)	115.938 (9)	87.740 (12)	721.62 (12)	4, 67
	8206	8.5878 (8)	12.9607 (15)	7.2197 (10)	90.590 (10)	115.950 (8)	87.738 (10)	721.98 (10)	4, 74

Bracketed quantities are uncertainties in the last decimal place(s) of the various parameters.

but still elutriated) and lower furnace temperatures in the early stages of homogenization (846°C first 48 h, 901°C next 130 h, 942°C last 74 h). A shorter homogenization time (252 h) and significantly less disordering during homogenization resulted. It appears that disordering in feldspar no. 8429 was comparable to that which took place in feldspars no. 8047 and no. 8205. Furthermore, a plot of $\cos \gamma$ versus $\cot \alpha^*$ (Thompson and Hovis, 1978) for the K-exchanged equivalents of these three feldspars indicates that the small degree of disordering that did take place was apparently between T_1 and T_2 tetrahedral sites (Z ordering), and not between T_1O and T_1m sites (Y ordering); in no. 8207 there is evidence for some degree of T_1O - T_1m disordering as well.

It is not known why sodic feldspars of the microcline series were affected by homogenization temperatures, while compositionally comparable feldspars of the topochemically monoclinic series were not. Perhaps the kinetics of disordering are increased for this series because its Al-Si distribution represents a temperature of equilibration lower than the temperatures represented by the Al-Si distributions of other series, thereby increasing the potential for disordering at homogenization temperatures that are well above equilibration temperatures for the series.

DETERMINATION OF LATTICE PARAMETERS

All feldspars were ground to fine powders and mixed with semiconductor-grade silicon ($a_0 = 5.43054 \text{ \AA}$; Parrish, 1960) as an internal standard. Unit-cell parameters were determined by least-squares refinement using the program LCLSQ of Burnham (1962). Uncertainties reported in Tables 5 and 6 are least-squares standard errors as calculated using Blasi's (1979) correction to

Burnham's program. Peaks of potassic feldspars and disordered analbite were indexed following data in Borg and Smith (1969). Peaks for crystalline solutions of intermediate composition, for ordered sodic feldspars, were indexed as previously described (Hovis, 1977, p. 674).

LATTICE PARAMETERS

Results

Direct and reciprocal lattice parameters for the four series of feldspars described above are listed in Table 6. In addition, data have been included for a fifth series based on topochemically monoclinic analbite. The lattice parameters for all members of the latter series except one (no. 7919) have been published previously (for seven members in Hovis, 1977, and for nos. 8001, 8008, and 8034 in Haselton et al., 1983). However, for internal consistency with the new feldspar series reported in this paper, all series members have been chemically reanalyzed by N. Suhr. Furthermore, volume errors reported in Hovis (1977) have been recalculated according to Blasi (1979). All members of the latter series originated from a specimen (no. 7015) made by disordering Amelia low albite at 1052°C for 710 h.

Henceforth it will be convenient to refer to the various series by the name of the endmember K-feldspars of each, such as "orthoclase" or "adularia" or "microcline." The two relatively disordered series will be referred to as the "Eifel sanidine" and "high sanidine" series.

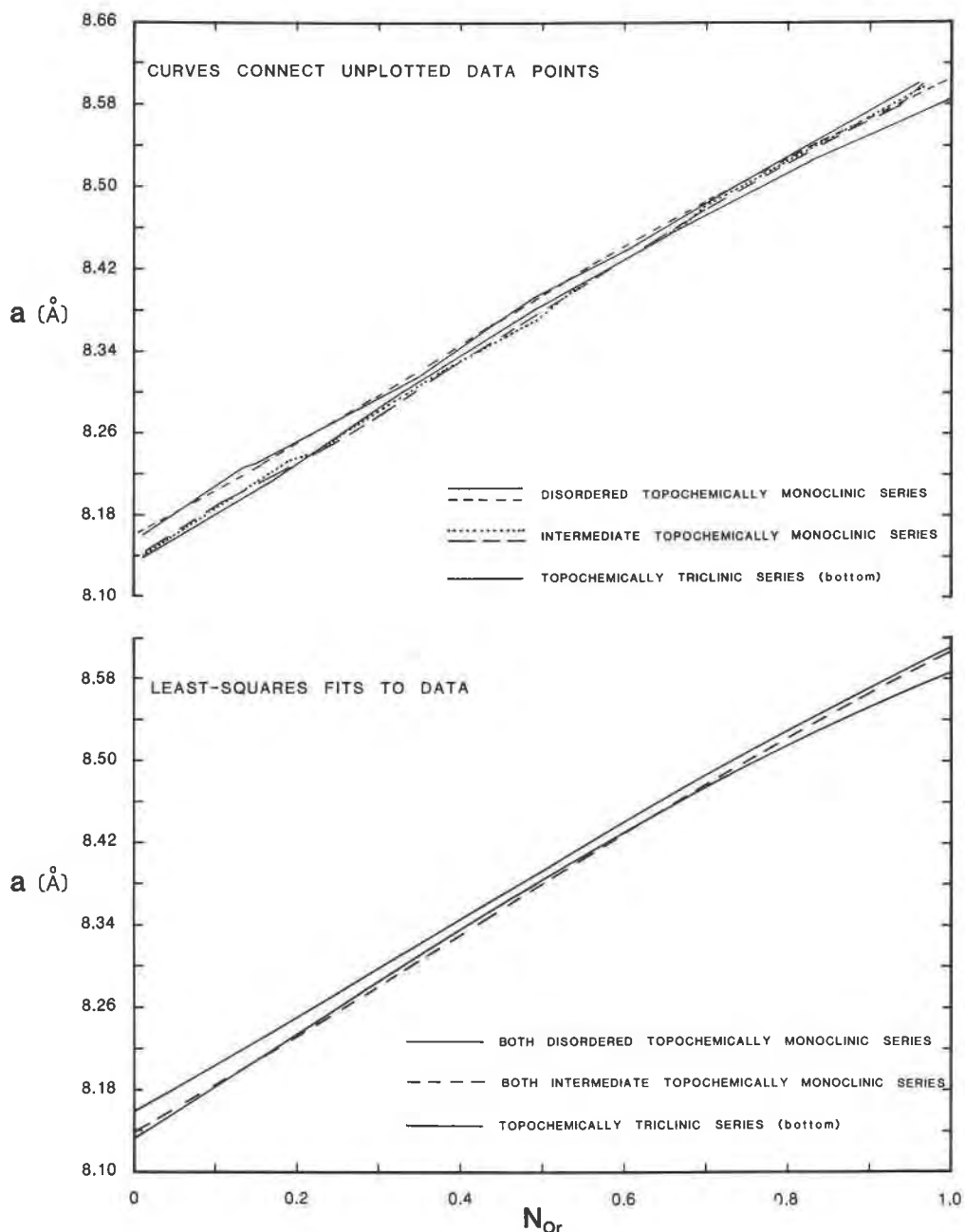


Fig. 1A (top). The a unit-cell dimension as a function of mole fraction KAlSi_3O_8 (N_{Or}) for the high sanidine (top solid curve), Eifel sanidine (short dashes), orthoclase (long dashes), adularia (dots), and microcline (this investigation; bottom solid curve) feldspar series. Curves shown do not represent least-squares fits to the data, but rather connect data points for individual series members. However, to improve clarity, the data points themselves are not shown. Note the extensive overlap between the two sanidine series and also between the orthoclase and adularia series.

Fig. 1B (bottom). The a unit-cell dimension plotted against composition. Curves represent least-squares fits to the data for the two sanidine series (top solid curve), the orthoclase and adularia series (dashes), and the microcline series of both this investigation and that of Orville (1967) (bottom solid curve) as expressed by Equations 2, 3, and 4.

Analysis of the data

In the discussion that follows, lattice-parameter data have been fit by the method of least-squares to equations having the form of simple power series:

$$y = a_0 + a_1N_{\text{Or}} + a_2N_{\text{Or}}^2 + \dots + a_nN_{\text{Or}}^n, \quad (1)$$

where n represents the degree of fit. Factors that will be taken into account in deciding which fits are to be used in a particular situation include (1) the Gauss criterion (Worthing and Geffner, 1943), (2) an overall view of how all series behave, as opposed to how a single series be-

Table 6. Lattice parameters for members of alkali feldspar ion-exchange series

Feldspar and Refinement	N_{Or}	a, a^* ($\text{\AA}, \text{\AA}^{-1}$)	b, b^* ($\text{\AA}, \text{\AA}^{-1}$)	c, c^* ($\text{\AA}, \text{\AA}^{-1}$)	α, α^* (deg)	β, β^* (deg)	γ, γ^* (deg)	V (\AA^3)	Scans, lines
High Sanidine Series									
7015	.0099	8.1617 (8)	12.8731 (11)	7.1117 (5)	93.479 (12)	116.450 (11)	90.211 (12)	667.36 (9)	3, 53
L0322T		.136930 (18)	.077871 (7)	.157435 (19)	86.008 (11)	63.482 (11)	88.030 (11)		
7059	.1437	8.2267 (11)	12.9174 (10)	7.1320 (5)	92.605 (11)	116.387 (7)	90.177 (12)	678.01 (9)	5, 100
L0323T		.135739 (19)	.077521 (6)	.156734 (12)	87.003 (10)	63.575 (7)	88.508 (11)		
8001	.1510	8.2315 (29)	12.9208 (23)	7.1312 (11)	92.555 (22)	116.358 (17)	90.093 (29)	678.74 (23)	3, 55
L0278T		.135618 (41)	.077494 (14)	.156699 (21)	87.102 (20)	63.609 (16)	88.629 (27)		
7919	.2753	8.2852 (14)	12.9602 (21)	7.1499 (6)	91.402 (14)	116.295 (9)	90.066 (17)	688.03 (13)	4, 56
L0324T		.134640 (24)	.077189 (12)	.156066 (14)	88.404 (12)	63.695 (9)	89.234 (15)		
7057	.3508	8.3174 (15)	12.9839 (15)	7.1576 (14)	90.0	116.164 (16)	90.0	693.77 (15)	6, 59
L0325T		.133955 (28)	.077018 (9)	.155661 (26)	90.0	63.836 (16)	90.0		
8008	.4406	8.3669 (9)	12.9927 (12)	7.1609 (8)	90.0	116.130 (8)	90.0	698.89 (9)	3, 53
L0279M		.133124 (15)	.076966 (7)	.155544 (12)	90.0	63.870 (8)	90.0		
7044	.4911	8.3929 (11)	12.9999 (13)	7.1653 (10)	90.0	116.104 (10)	90.0	702.04 (10)	3, 56
L0326M		.132682 (18)	.076923 (8)	.155414 (15)	90.0	63.896 (10)	90.0		
7058	.5993	8.4368 (11)	13.0155 (13)	7.1660 (10)	90.0	116.020 (10)	90.0	707.13 (10)	3, 47
L0327M		.131897 (18)	.076831 (7)	.155288 (16)	90.0	63.980 (10)	90.0		
8034	.7333	8.4991 (10)	13.0209 (14)	7.1703 (8)	90.0	116.004 (8)	90.0	713.17 (10)	3, 60
L0285M		.130913 (17)	.076800 (9)	.155173 (16)	90.0	63.996 (8)	90.0		
7060	.8074	8.5334 (7)	13.0295 (9)	7.1752 (7)	90.0	115.992 (7)	90.0	717.09 (7)	4, 92
L0328M		.130373 (12)	.076749 (6)	.155051 (12)	90.0	64.008 (7)	90.0		
7036	.9600	8.6013 (10)	13.0312 (13)	7.1783 (8)	90.0	115.992 (9)	90.0	723.20 (10)	3, 78
L0329M		.129344 (15)	.076739 (7)	.154984 (15)	90.0	64.008 (9)	90.0		
Eifel Sanidine Series									
71102	.0029	8.1634 (10)	12.8630 (15)	7.1173 (8)	93.337 (12)	116.447 (9)	90.296 (11)	667.61 (9)	3, 58
L0443T		.136900 (18)	.077921 (9)	.157285 (19)	86.125 (10)	63.484 (9)	88.006 (10)		
72003	.1553	8.2288 (15)	12.9155 (13)	7.1389 (8)	92.483 (15)	116.383 (12)	90.214 (16)	678.83 (13)	3, 58
L0442T		.135698 (26)	.077525 (8)	.156561 (21)	87.122 (13)	63.580 (11)	88.528 (14)		
8201	.2898	8.2921 (16)	12.9643 (21)	7.1584 (9)	90.898 (32)	116.266 (22)	90.118 (21)	689.96 (23)	6, 59
L0417T		.134489 (43)	.077148 (13)	.155808 (34)	88.940 (34)	63.729 (22)	89.425 (24)		
8202	.4346	8.3646 (7)	12.9867 (8)	7.1678 (4)	90.0	116.129 (5)	90.0	699.05 (6)	4, 81
L0418T		.133159 (11)	.077002 (5)	.155393 (8)	90.0	63.871 (5)	90.0		
72001B	.5557	8.4223 (9)	12.9977 (11)	7.1710 (8)	90.0	116.049 (7)	90.0	705.27 (8)	3, 72
L0319M		.132158 (14)	.076936 (6)	.155219 (12)	90.0	63.951 (7)	90.0		
8203	.7083	8.4890 (8)	13.0110 (10)	7.1759 (8)	90.0	115.995 (7)	90.0	712.41 (8)	4, 107
L0419M		.131058 (10)	.076858 (6)	.155039 (13)	90.0	64.005 (7)	90.0		
7002	.8359	8.5425 (8)	13.0195 (11)	7.1829 (7)	90.0	115.994 (7)	90.0	718.05 (8)	3, 91
L0318M		.130237 (13)	.076808 (7)	.154889 (11)	90.0	64.006 (7)	90.0		
7052	.9917	8.6024 (7)	13.0202 (9)	7.1875 (5)	90.0	115.996 (6)	90.0	723.59 (7)	3, 120
L0317M		.129332 (9)	.076804 (5)	.154792 (10)	90.0	64.004 (6)	90.0		
Orthoclase Series									
8431	.0135	8.1435 (12)	12.8377 (16)	7.1314 (7)	93.307 (14)	116.516 (10)	90.302 (14)	665.61 (11)	6, 80
L0512T		.137316 (23)	.078072 (10)	.157062 (19)	86.152 (11)	63.417 (10)	88.010 (12)		
7735	.1101	8.1944 (14)	12.8810 (10)	7.1486 (5)	92.740 (12)	116.447 (8)	90.226 (12)	674.55 (11)	4, 79
L0306T		.136352 (23)	.077753 (6)	.156477 (10)	86.827 (11)	63.508 (7)	88.383 (11)		
7818	.2376	8.2470 (21)	12.9129 (15)	7.1633 (5)	91.698 (14)	116.408 (13)	90.147 (17)	682.83 (16)	4, 56
L0307T		.135404 (30)	.077488 (9)	.155958 (18)	88.031 (12)	63.574 (14)	88.992 (15)		
7815	.3021	8.2780 (9)	12.9348 (18)	7.1735 (8)	90.853 (26)	116.337 (13)	89.931 (35)	688.28 (15)	7, 47
L0308T		.134796 (19)	.077321 (11)	.155569 (26)	89.083 (22)	63.661 (13)	89.655 (32)		
7906	.3814	8.3217 (9)	12.9476 (10)	7.1761 (12)	90.0	116.278 (10)	90.0	693.29 (11)	4, 54
L0309M		.134017 (20)	.077234 (6)	.155412 (27)	90.0	63.722 (10)	90.0		
7905	.4652	8.3618 (12)	12.9548 (13)	7.1792 (11)	90.0	116.173 (11)	90.0	697.95 (11)	3, 68
L0310M		.133254 (21)	.077192 (8)	.155205 (15)	90.0	63.827 (11)	90.0		
7801	.5707	8.4149 (9)	12.9710 (9)	7.1841 (6)	90.0	116.100 (7)	90.0	704.18 (7)	3, 83
L0311M		.132331 (15)	.077095 (5)	.155002 (12)	90.0	63.900 (7)	90.0		
7908	.6981	8.4781 (7)	12.9798 (9)	7.1889 (6)	90.0	116.058 (7)	90.0	710.68 (7)	3, 62
L0312M		.131298 (11)	.077043 (5)	.154843 (10)	90.0	63.942 (7)	90.0		
7903	.7885	8.5174 (8)	12.9879 (10)	7.1947 (6)	90.0	116.042 (6)	90.0	715.09 (7)	3, 89
L0313M		.130673 (14)	.076995 (6)	.154697 (12)	90.0	63.958 (6)	90.0		
7814	.8719	8.5558 (8)	12.9877 (10)	7.1959 (6)	90.0	116.032 (6)	90.0	718.49 (7)	3, 86
L0314M		.130076 (12)	.076996 (6)	.154658 (11)	90.0	63.968 (6)	90.0		
B1893B	.9343	8.5782 (9)	12.9879 (12)	7.1971 (8)	90.0	116.036 (8)	90.0	720.48 (9)	3, 91
L0315M		.129741 (16)	.076995 (7)	.154637 (15)	90.0	63.964 (8)	90.0		
7738	.9649	8.6011 (11)	12.9945 (12)	7.2021 (7)	90.0	116.044 (8)	90.0	723.22 (10)	2, 66
L0316M		.129404 (15)	.076956 (7)	.154541 (11)	90.0	63.956 (8)	90.0		

have, and (3) not only whether using a higher-order fit lowers the standard deviation in a particular situation, but whether the standard deviation of fit is lowered substantially. Note that feldspar series with small numbers of data points, in this case the microcline and Eifel sanidine series, may not include enough data points to give a valid reading of the best least-squares fit for a particular pair of parameters. In some cases the tendency for such a series is for the standard deviation of fit to steadily decline until an exact fit is reached (e.g., a sixth-order fit for seven data points).

Length of a axis

Values of a determined for the five feldspar series of this investigation are plotted against composition in Fig-

ure 1A (compare with Kroll and Ribbe, 1983, Fig. 2). Three trends are apparent, one for the two sanidine series, one for the orthoclase and adularia series, and one for the microcline series. Both sanidine series begin at sodic compositions with a values that are between 0.02 and 0.03 \AA greater than for any of the other series. Moreover, a distinct difference in a values between these two series and the microcline series is maintained over the entire compositional range. On the other hand, the difference between the two sanidine series and the orthoclase and adularia series is maintained only between N_{Or} values of 0.0 and 0.7. Above the latter composition, the orthoclase-adularia trend merges with that of the sanidines. It is apparent, then, that values of a are affected by Al/Si distribution to a small but significant degree.

Table 6—Continued

Feldspar and Refinement	N_{Or}	a, a^* (Å, Å ⁻¹)	b, b^* (Å, Å ⁻¹)	c, c^* (Å, Å ⁻¹)	α, α^* (deg)	β, β^* (deg)	γ, γ^* (deg)	V (Å ³)	Scans, lines
Adularia Series									
7190	.0103	8.1407 (14)	12.8244 (18)	7.1450 (8)	93.145 (17)	116.549 (10)	90.250 (17)	665.92 (12)	3, 59
L0289T		.137392 (24)	.078135 (11)	.156773 (20)	86.359 (13)	63.392 (10)	88.147 (13)		
7197	.0753	8.1754 (16)	12.8468 (19)	7.1536 (10)	92.825 (18)	116.517 (11)	90.221 (18)	671.19 (13)	2, 45
L0290T		.136757 (26)	.077968 (11)	.156479 (22)	86.732 (15)	63.436 (11)	88.342 (15)		
7927	.1879	8.2336 (11)	12.8832 (12)	7.1663 (9)	91.920 (12)	116.453 (8)	90.130 (13)	680.07 (9)	4, 64
L0291T		.135681 (20)	.077679 (7)	.155977 (16)	87.790 (10)	63.526 (8)	88.898 (11)		
73011E	.2308	8.2441 (40)	12.8993 (43)	7.1718 (21)	91.523 (27)	116.389 (28)	90.111 (32)	682.88 (30)	5, 48
L0292T		.135425 (59)	.077560 (26)	.155727 (49)	88.245 (25)	63.598 (28)	89.120 (30)		
7917	.2585	8.2619 (21)	12.9081 (18)	7.1792 (11)	90.935 (22)	116.355 (25)	90.063 (39)	685.92 (17)	6, 57
L0293T		.135083 (22)	.077485 (11)	.155477 (36)	88.926 (24)	63.640 (25)	89.467 (41)		
73013E	.3835	8.3234 (15)	12.9305 (13)	7.1855 (21)	90.0	116.210 (16)	90.0	693.84 (17)	5, 52
L0294M		.133912 (29)	.077337 (8)	.155117 (40)	90.0	63.790 (16)	90.0		
7914	.4917	8.3716 (14)	12.9379 (14)	7.1948 (11)	90.0	116.169 (12)	90.0	699.40 (13)	3, 50
L0296M		.133094 (21)	.077293 (8)	.154863 (21)	90.0	63.831 (12)	90.0		
7196C	.5365	8.3996 (9)	12.9494 (12)	7.1970 (6)	90.0	116.116 (7)	90.0	702.89 (8)	3, 76
L0297M		.132590 (15)	.077224 (7)	.154746 (11)	90.0	63.884 (7)	90.0		
7918	.6776	8.4648 (11)	12.9548 (15)	7.2003 (10)	90.0	116.028 (9)	90.0	709.51 (10)	3, 67
L0298M		.131470 (17)	.077192 (9)	.154557 (17)	90.0	63.972 (9)	90.0		
7007	.8602	8.5509 (11)	12.9656 (15)	7.2075 (9)	90.0	116.037 (10)	90.0	717.98 (10)	3, 64
L0300M		.130155 (19)	.077127 (9)	.154415 (13)	90.0	63.963 (10)	90.0		
7198	.8602	8.5485 (7)	12.9688 (9)	7.2057 (6)	90.0	116.009 (6)	90.0	717.95 (7)	2, 65
L0301M		.130161 (10)	.077108 (6)	.154418 (11)	90.0	63.991 (6)	90.0		
7049	.9682	8.5974 (5)	12.9706 (8)	7.2118 (4)	90.0	116.027 (4)	90.0	722.66 (5)	4, 124
L0303M		.129441 (8)	.077097 (5)	.154311 (7)	90.0	63.973 (4)	90.0		
7045	.9972	8.5963 (9)	12.9709 (14)	7.2123 (10)	90.0	116.038 (9)	90.0	722.57 (11)	3, 92
L0302M		.129470 (14)	.077095 (9)	.154314 (19)	90.0	63.962 (9)	90.0		
Microcline Series									
7010	.0099	8.1397 (11)	12.7867 (13)	7.1592 (6)	94.251 (12)	116.597 (9)	87.679 (9)	664.43 (9)	4, 79
L0426T		.137398 (21)	.078425 (8)	.156518 (14)	86.407 (12)	63.493 (9)	90.470 (9)		
8205	.1695	8.2188 (19)	12.8315 (23)	7.1693 (8)	93.521 (15)	116.344 (14)	87.791 (13)	676.22 (12)	6, 85
L0511T		.135783 (30)	.078087 (14)	.155840 (21)	87.164 (13)	63.733 (14)	90.723 (10)		
8207	.3311	8.3013 (16)	12.8926 (16)	7.1857 (6)	92.434 (17)	116.192 (35)	87.870 (13)	689.31 (21)	6, 68
L0440T		.134276 (45)	.077650 (9)	.155157 (47)	88.334 (19)	63.864 (35)	91.178 (17)		
8429	.3337	8.2997 (12)	12.8882 (14)	7.1882 (7)	92.630 (12)	116.115 (13)	87.695 (12)	689.52 (10)	4, 62
L0509T		.134218 (15)	.077691 (9)	.155009 (17)	88.200 (13)	63.951 (13)	91.279 (13)		
8047	.4926	8.3825 (18)	12.9345 (15)	7.2006 (12)	91.496 (13)	115.987 (14)	87.685 (12)	701.17 (15)	4, 75
L0429T		.132784 (27)	.077379 (9)	.154505 (24)	89.463 (13)	64.048 (14)	91.846 (12)		
8204	.6553	8.4538 (10)	12.9496 (13)	7.2102 (4)	91.054 (7)	115.920 (6)	87.585 (7)	709.29 (7)	4, 68
L0430T		.131615 (14)	.077291 (8)	.154206 (9)	90.001 (7)	64.100 (6)	92.172 (7)		
8206	.8295	8.5262 (10)	12.9607 (14)	7.2134 (9)	90.747 (11)	115.919 (8)	87.664 (11)	716.34 (10)	4, 100
L0431T		.130502 (16)	.077221 (8)	.154137 (19)	90.304 (11)	64.089 (8)	92.234 (10)		
71104	.9972	8.5861 (7)	12.9565 (12)	7.2198 (8)	90.611 (8)	115.931 (6)	87.672 (8)	721.69 (8)	10, 172
L0473T		.129609 (9)	.077248 (7)	.154019 (16)	90.452 (8)	64.072 (7)	92.291 (8)		

Bracketed quantities are uncertainties in the last decimal place(s) of the various parameters.

Best least-squares fits for a - N_{Or} relations in the various ion-exchange series are given in Table 7.

Indirect determination of composition. The a unit-cell dimension has commonly been used to indirectly determine the Ab and Or contents of alkali feldspars. Generally, linear equations have been given for the relationship between a and N_{Or} (including Hovis, 1977). There is no question that such equations give good approximations of composition, but for some applications such as thermodynamic and phase-equilibrium calculations, maximum precision is necessary. New data of this investigation provided the opportunity to test whether a is a linear function of N_{Or} and to develop equations for feldspars having different Al-Si distributions.

Least-squares analysis of data for nine feldspar series (Table 8), including the five discussed in this paper (coefficients in Table 7), gives linear fits as the best fits in only two cases. When data of feldspars with similar structures are combined (microclines, orthoclase-adularia, and sanidines), the best fits are still nonlinear. Although no clear picture emerges as to which order of fit is generally best, at least a cubic fit is required based on the fits to combined data. This is also consistent with the pattern seen in eight of the nine individual series, which require upward concavity at sodic compositions and downward concavity at potassic compositions (quadratic equations do not allow

a change in the curvature of a - N_{Or} relations). For the determination of N_{Or} content where the highest precision and internal consistency is important, therefore, linear equations suggested in the past should be replaced by the following: For disordered feldspars,

$$N_{Or} = -1362.802 + 486.4938a - 58.11977a^2 + 2.324427a^3; \quad (2)$$

for ordered topochemically monoclinic feldspars (orthoclase and monoclinic adularia),

$$N_{Or} = -366.3261 + 129.2335a - 15.42053a^2 + 0.6232109a^3; \quad (3)$$

and for topochemically triclinic feldspars,

$$N_{Or} = -657.3958 + 239.9022a - 29.40843a^2 + 1.211078a^3. \quad (4)$$

The large number of significant figures in these equations is required to avoid round-off error. Curves representing these equations are shown in Figure 1B. All equations should be applied only to unstrained feldspars.

Length of b axis

The b unit-cell dimension (Fig. 2) is strongly affected by both composition and Al-Si distribution. From mi-

Table 7. Least-squares equations for the a unit-cell dimension as a function of N_{Or} for feldspar series of this investigation

Feldspar series	Least-squares coefficients				
	a_0	a_1	a_2	a_3	a_4
High sanidine	8.1574 (.0017)	0.47768 (.0082)	-0.015435 (.0082)		
Eifel sanidine	8.1623 (.0010)	0.37482 (.016)	0.40075 (.073)	-0.53518 (.11)	0.20295 (.057)
Orthoclase	8.1379 (.0015)	0.47922 (.0024)			
Adularia	8.1357 (.0029)	0.53885 (.042)	-0.31683 (.18)	0.59077 (.27)	-0.34729 (.13)
Microcline	8.1345 (.0026)	0.48964 (.025)	0.06672 (.060)	-0.10443 (.039)	

Equations have the form:
 $a(A) = a_0 + a_1N_{Or} + a_2N_{Or}^2 + a_3N_{Or}^3 + a_4N_{Or}^4$
 Bracketed quantities are uncertainties in the calculated coefficients. The number of significant figures stated for the coefficients are high relative to the uncertainties, but this is necessary to avoid roundoff error for those who may wish to use the equations.

crocline through the intermediate series to high sanidine, b increases as Al and Si become more disordered. All series have concave down trends with composition, but it is important for later discussions to note that b becomes nearly constant above N_{Or} values of about 0.75.

Stewart (1975) noted that the plots of various unit-cell parameters against composition seem to change slope abruptly at an N_{Or} value of ~ 0.4 (see also Stewart and Wright, 1974). We have noted the same phenomenon in a separate phase-equilibrium investigation (Hovis, Delbove, and Roll, in prep.) involving two series of feldspars and a considerably larger number of data points than for any single series reported in this paper. The break in slope is especially evident on plots of b versus N_{Or} and c versus N_{Or} and seems to occur near the composition ($N_{Or} = 0.29$ to 0.35, depending on the series) of the triclinic-monoclinic displacive transformation of topochemically monoclinic feldspar series. It was appropriate, therefore, to analyze the variation of b separately for monoclinic versus triclinic parts of the four topochemically monoclinic se-

ries. Displacive transformation compositions were determined for each series using the parameter $(1 - \cos \phi)$ (Hovis, 1980).

In the triclinic part of the compositional range, least-squares analyses of b indicated that linear fits were best—or at least could not be substantially improved upon—for

Table 8. Best orders of least-squares fits for a as a function of N_{Or} for various feldspar series

Feldspar series	Order of best fit	Sequence of standard deviations of fit from first order to best order (Å)
High sanidine (this investigation)	2	.0031, .0030
Eifel sanidine (this investigation)	4	.0062, .0044, .0019, .0008
Combined high sanidine and Eifel sanidine series (this investigation)	3	.0047, .0039, .0033
Orthoclase series (this investigation)	1	.0036
Adularia series (this investigation)	4	.0058, .0050, .0045, .0040
Combined orthoclase and adularia series (this investigation)	4	.0051, .0046, .0040, .0038
Microcline series (this investigation)	3	.0107, .0039, .0022
Microcline series (Orville, 1967)	2	.0101, .0046
Combined microcline series of this investigation and Orville (1967)	6	.0097, .0039, .0036, .00314, .00310, .00309
High sanidine series (Orville, 1967)	1	.0061
Orthoclase series (Wright and Stewart, 1968)	3	.0052, .0050, .0038
Microcline series (Hovis and Peckins, 1978)	4	.0078, .0077, .0041, .0035

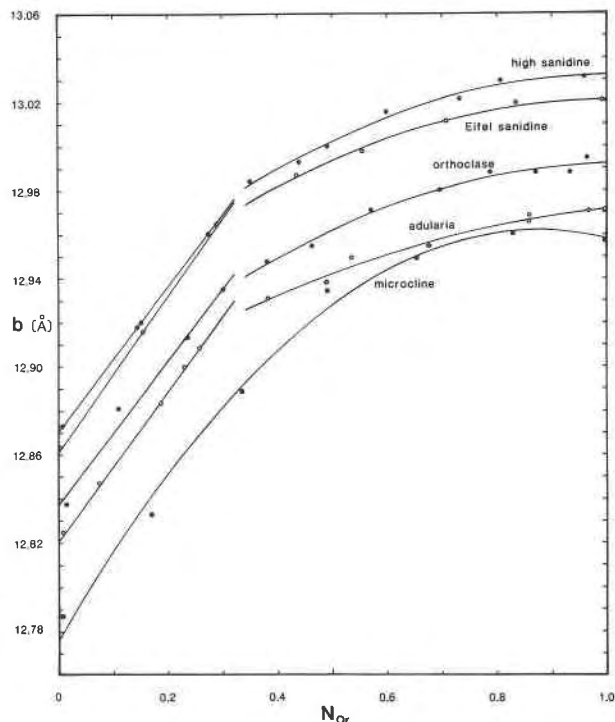


Fig. 2. The b unit-cell dimension as a function of N_{Or} . Data for topochemically monoclinic feldspars are shown as circles, alternating as solid and open from the high sanidine series to the adularia series. Microcline data are shown as solid squares. Equations for lines and curves fit through the data are given in Table 9. For topochemically monoclinic series, lines and curves for triclinic (sodic) and monoclinic (potassic) compositional regions are shown, whereas for the microcline series, the quadratic least-squares fit for the entire series is shown. When microcline data from Orville (1967) are combined with those of the present study, a higher-order fit is appropriate to accommodate concave-up relationships at sodic compositions and concave-down relationships at potassic compositions; a fourth-order fit is assumed in Fig. 10.

Table 9. Least-squares equations for b and c unit-cell dimensions as a function of N_{Or} for feldspar series of this investigation

Series and compositional region	Unit-cell parameter (\AA)	Least-squares coefficients			Standard deviation of fit (\AA)
		a_0	a_1	a_2	
High sanidine, triclinic	b	12.8703 (.0010)	0.3284 (.0061)		0.0008
	c	7.1104 (.0012)	0.1438 (.0070)		0.0009
High sanidine, monoclinic	b	12.9153 (.011)	0.2312 (.037)	-0.1143 (.028)	0.0026
	c	7.1466 (.0015)	0.0336 (.0023)		0.0014
Eifel sanidine, triclinic	b	12.8615 (.0019)	0.3533 (.010)		0.0010
	c	7.1168 (.0003)	0.1434 (.0017)		0.0002
Eifel sanidine, monoclinic	b	12.9123 (.017)	0.2157 (.050)	-0.1071 (.035)	0.0018
	c	7.1511 (.0021)	0.0368 (.0028)		0.0011
Orthoclase, triclinic	b	12.8379 (.0080)	0.3241 (.040)		0.0064
	c	7.1308 (.0025)	0.1413 (.013)		0.0020
Orthoclase, monoclinic	b	12.8764 (.012)	0.2255 (.038)	-0.1101 (.028)	0.0027
	c	7.1600 (.0014)	0.0419 (.0019)		0.0013
Adularia, triclinic	b	12.8210 (.0007)	0.3365 (.0041)		0.0008
	c	7.1434 (.0018)	0.1296 (.0099)		0.0018
Adularia, monoclinic	b	12.8770 (.012)	0.1657 (.036)	-0.0714 (.026)	0.0027
	c	7.1737 (.0019)	0.0390 (.0025)		0.0019
Microcline, sodic	b	12.7818 (.0080)	0.3134 (.037)		0.0004
	c	7.1569 (.0065)	0.0896 (.030)		0.0034
Microcline, potassic	b	12.8257 (.043)	0.3057 (.12)	-0.1746 (.080)	0.0022
	c	7.1843 (.0058)	0.0359 (.0075)		0.0020
Microcline, whole series	b	12.7765 (.0065)	0.4239 (.030)	-0.2429 (.029)	0.0072
	c	7.1559 (.0025)	0.1115 (.012)	-0.0479 (.011)	0.0028

Equations have the form:

$$b \text{ (or } c) = a_0 + a_1 N_{Or} + a_2 N_{Or}^2$$

Bracketed quantities are uncertainties in the calculated coefficients. The number of significant figures stated for the coefficients are high relative to the uncertainties, but this is necessary to avoid roundoff error for those who may wish to use the equations.

all three of the topochemically monoclinic series in which a quadratic fit did not represent an exact fit to the data. Furthermore, the $\Delta b/\Delta N_{Or}$ slopes of the lines for various series were quite similar and nearly within the statistical uncertainties of each other (Table 9). Even the microcline series (which cannot undergo a monoclinic-triclinic transformation), with its three most sodic members fit separately, yielded a slope almost identical to those of the other four series.

Monoclinic parts of the four topochemically monoclinic series all require at least a quadratic least-squares fit of b as a function of N_{Or} . In no case would a cubic equation significantly improve the standard deviation of the least-squares fit. Curvature of the two sanidine series and the orthoclase series are similar, while the curve for the adularia series is somewhat flatter.

The potassic part of our microcline series is more strongly curved than that of the other series, and there is some suggestion for this series that b may go through a maximum and then decrease slightly at the K end, although this is not substantiated by the data of Orville (1967), or the unpublished data of Kroll (in Kroll and Ribbe, 1983; also see Kroll et al., 1986). At the very least, b does level off at K-rich compositions. There are small differences in b between the microcline series reported here and Orville's. These cannot be due to small degrees of disordering during homogenization, because they occur mainly in the potassic part of the compositional range where such effects are clearly either nonexistent or at least minimal, but must be due to other factors such as data selection for the refinements.

Because separate relationships of b vs. N_{Or} have been calculated for triclinic and monoclinic parts of each topochemically monoclinic feldspar series, it is possible to

calculate the compositions at which they intersect, thus predicting the N_{Or} values at which the triclinic/monoclinic transformations take place. The transformation N_{Or} values so calculated are within 0.02 of those predicted from the earlier-used $(1 - \cos \phi)$ parameter (Hovis, 1980).

Length of c axis

The c unit-cell dimension (Fig. 3) is also strongly affected by both composition and ordering. As a feldspar becomes disordered its c parameter decreases. The variation of c across any one of the series produces a concave-down c - N_{Or} trend. Unlike b , however, c continues to increase to the K end of each series. This, combined with the tendency of b to become constant for potassic feldspars, means that a plot of b against c , commonly used to determine Al-Si distributions, will produce a nearly vertical tail at the potassic ends of ion exchange series.

Just as for b , the variation of c was analyzed separately for the triclinic and monoclinic segments of all topochemically monoclinic series. In the triclinic part of the compositional range, linear least-squares fits were generally best (Table 9) as an expression of c - N_{Or} relations. The $\Delta c/\Delta N_{Or}$ slopes of these lines all are within the combined uncertainties of each other (see coefficients in Table 9). Unlike b , c also behaves linearly in the monoclinic regions of these series. Only in the case of the adularia series did a quadratic equation lower the standard deviation of fit, and in that case improvement was minimal. Here, too, $\Delta c/\Delta N_{Or}$ slopes (coefficient a_1 of Table 9) are within the combined uncertainties of each other (except if comparing the high sanidine and orthoclase series) and have an average value of $0.038 \pm 0.003 \text{ \AA}$. The linear behavior of c in both the triclinic and monoclinic compositional regions of these series, as well as the constant $\Delta c/\Delta N_{Or}$ slopes

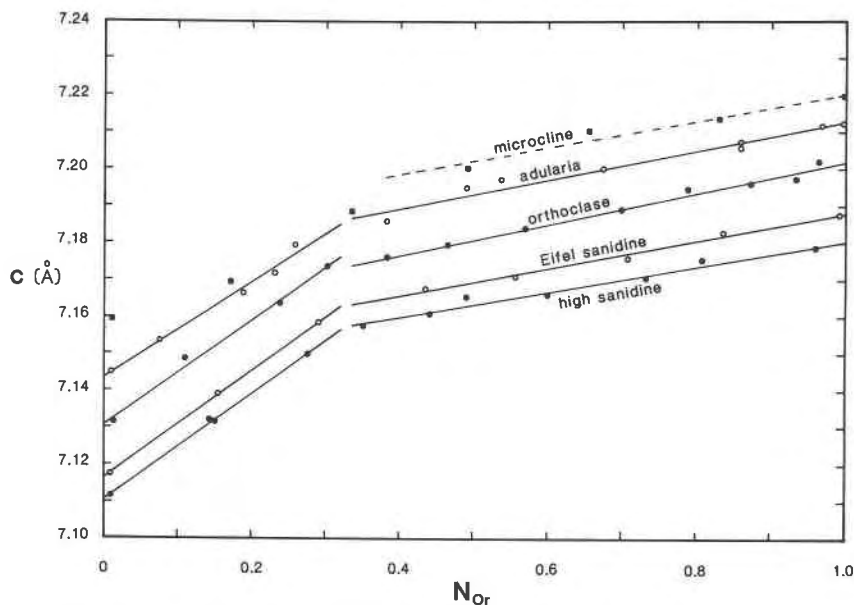


Fig. 3. The c unit-cell dimension as a function of N_{or} . Data for topochemically monoclinic feldspars are shown as circles, alternating as solid and open from the high sanidine series to the adularia series. Microcline data are shown as solid squares. For topochemically monoclinic series, linear least-squares fits are shown for both triclinic and monoclinic segments of the series (see equations of Table 9). Note the similarity in slopes among all series. For the microcline series, only a linear fit of the data for $N_{or} > 0.4$ is shown, to emphasize its similarity to the other series.

from series to series, makes the c dimension a primary candidate as an ordering parameter in alkali feldspars. Again, N_{or} values for the triclinic-monoclinic transition determined by the intersection of monoclinic and triclinic c - N_{or} lines agree well with those using the $(1 - \cos \phi)$ parameter.

Even though the microcline series does not undergo a triclinic-monoclinic transformation, parallels can be drawn between its behavior and that of the topochemically monoclinic series, particularly at K-rich compositions. If one fits by least squares the four most potassic data points ($N_{or} > 0.49$) only, c - N_{or} relations are linear, and $\Delta c/N_{or}$ is $0.036 \pm 0.008 \text{ \AA}$, virtually identical to that of the other series. A similar approach to Orville's (1967) microcline series for data at $N_{or} > 0.48$ yields a linear fit and a slope of $0.039 \pm 0.003 \text{ \AA}$ (or for $N_{or} > 0.38$ a linear fit and slope of $0.040 \pm 0.003 \text{ \AA}$). Thus, the usefulness of c as an ordering parameter is extended to topochemically triclinic series.

With only three data points at the sodic end ($N_{or} < 0.034$) of the microcline series, no test could be made for nonlinearity of the data. The $\Delta c/\Delta N_{or}$ slope of the linear fit yielded a slope of $0.090 \pm 0.030 \text{ \AA}$, shallower than those of the topochemically monoclinic series. A similar treatment to sodic members of Orville's (1967) microcline series also yielded shallower slopes than for topochemically monoclinic series. It is likely, however, that nonlinear fits are a better choice for c - N_{or} relations in the sodic regions of microcline series. If individually fit to quadratic equations, the data of both Orville (1967) and the present series yield concave-up relations in this region. The un-

published data of Kroll (see c - N_{or} plot of Fig. 2, p. 72, in Kroll and Ribbe, 1983) agree with this.

Because the microcline series does not undergo a triclinic-monoclinic transformation, it is also reasonable to treat both b and c as continuous functions across the entire compositional region. Coefficients for these equations also are included in Table 9.

Interaxial angles

The four topochemically monoclinic alkali feldspar series have non- 90° α and γ values only in the sodic third of their compositional ranges (Fig. 4) owing to the triclinic-monoclinic displacive transformation in these series. Over this range, α is sensitive to ordering within the topochemically monoclinic series to a very small degree, with the high sanidine series having slightly higher and the adularia series slightly lower values of α than the other two series. In the microcline series, α has distinctly higher values than in the other series and varies as indicated previously (e.g., Orville, 1967; Hovis and Peckins, 1978; Thompson and Hovis, 1978). The γ value is relatively insensitive to both composition and ordering within the topochemically monoclinic series; in the microcline series, γ has distinctly lower values that hardly vary with composition. Because of the behavior of α and γ , the plot of $\cos \gamma$ vs. $\cot \alpha^*$ devised by Thompson and Hovis (1978) shows the four topochemically monoclinic series to be virtually inseparable, whereas the microcline series has a distinct trend of its own, very similar to Figure 7 of the aforementioned paper.

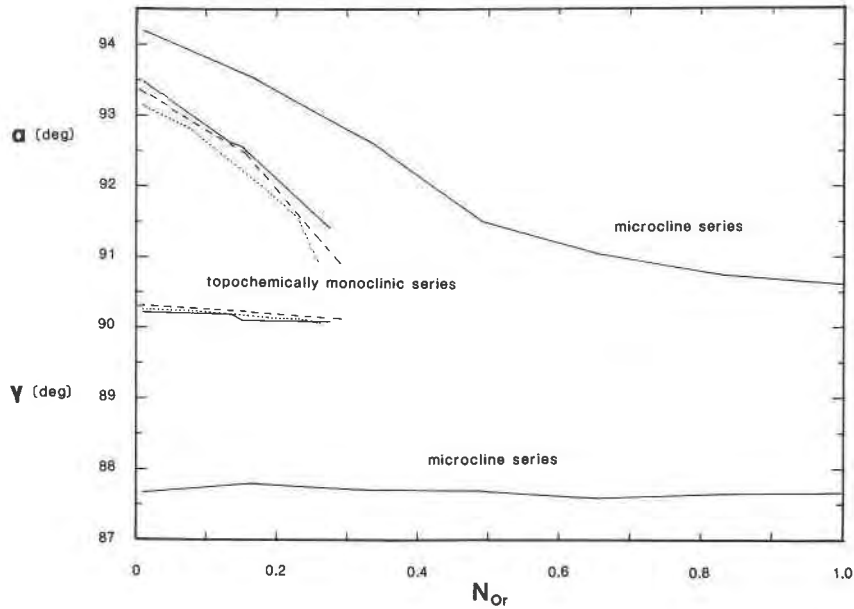


Fig. 4. Variation of the α and γ interaxial angles as functions of N_{Or} . Curves are not least-squares fits to the data, but rather connect data points for individual series members. For clarity, individual data points are not shown, and only three of the topochemically monoclinic feldspars are represented, the high sanidine series (solid curve), the orthoclase series (dashes), and the adularia series (dots).

The β interaxial angle has a concave-up relationship with composition for all five feldspar series (Fig. 5). This parameter has a higher value at the sodic (low albite) end of the microcline series than that for any of the topochemically monoclinic series. However, it rapidly decreases with K content and has lower values for low albite-microcline members than for members of other series over

most of the compositional range. Within the topochemically monoclinic series, β is somewhat sensitive to ordering, the adularia and orthoclase series generally having higher values of β than those for members of the two sanidine series. Fourth-order β - N_{Or} relationships are given in Table 10 since these represent the lowest standard deviations of fit for four of the five series.

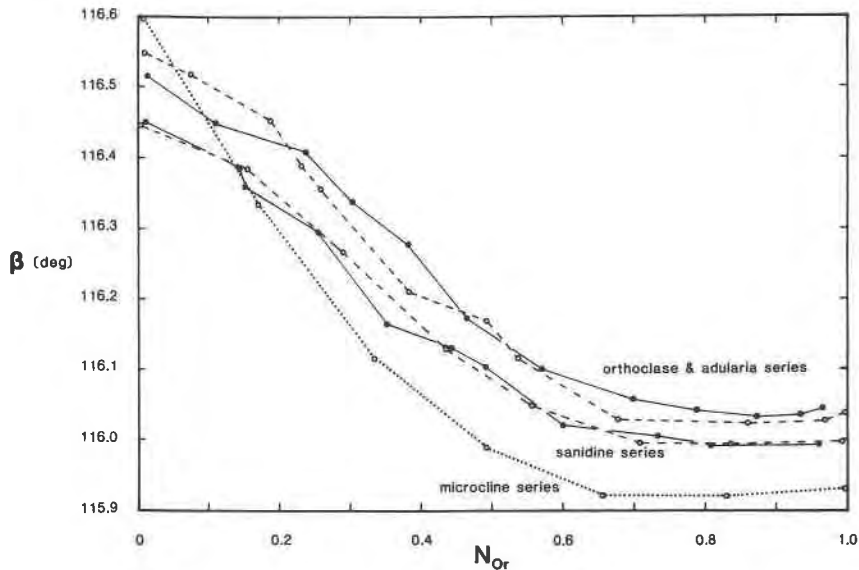


Fig. 5. The β interaxial angle as a function of N_{Or} . Solid circles and the solid curve at the top are for the orthoclase series, open circles and dashes are for adularia. Lower solid circles and solid curve are for the high sanidine series, and overlapping open circles and dashes are for Eifel sanidine. Open squares and the dotted curve represent data from the microcline series.

Table 10. Least-squares equations for β as a function of N_{Or} for feldspar series of this investigation

Feldspar series	Least-squares coefficients					Standard deviation of fit (deg)
	a_0	a_1	a_2	a_3	a_4	
High sanidine	116.450 (.019)	-0.1366 (.28)	-3.150 (1.2)	4.995 (1.9)	-2.170 (1.0)	0.021
Eifel sanidine	116.446 (.003)	0.0979 (.048)	-4.079 (.22)	6.165 (.34)	-2.635 (.17)	0.002
Orthoclase	116.504 (.015)	0.0746 (.24)	-3.268 (1.1)	4.275 (1.7)	-1.533 (.84)	0.018
Adularia	116.552 (.013)	-0.1929 (.19)	-3.187 (.80)	4.779 (1.2)	-1.916 (.60)	0.018
Microcline	116.614 (.009)	-1.646 (.16)	-0.2313 (.70)	2.724 (1.1)	-1.530 (.54)	0.006

Equations have the form:

$$\beta \text{ (deg)} = a_0 + a_1 N_{Or} + a_2 N_{Or}^2 + a_3 N_{Or}^3 + a_4 N_{Or}^4$$
 Bracketed quantities are uncertainties in the calculated coefficients. The number of significant figures stated for the coefficients are high relative to the uncertainties, but this is necessary to avoid roundoff error for those who may wish to use the equations.

Reciprocal cell dimensions

The behavior of reciprocal cell dimensions is largely analogous to that of the direct cell dimensions. Their variations with composition are shown in Figures 6 and 7.

Unit-cell volumes as indicators of composition

Unit-cell volumes for series members are included in Table 6 and plotted in Figure 8A. A detailed analysis of volumes as thermodynamic parameters will be made in a second paper (Hovis, in prep.). However, inspection of Figure 8A indicates that they are functions of both composition and Al-Si distribution. The two sanidine series have volumes that are generally higher than those of any of the other series. Volumes of the orthoclase and adularia series repeatedly cross each other and, at most compositions, are between those of the other series. Volumes of the microcline series are lower than any of the other four series at values of $N_{Or} < 0.4$ and $N_{Or} > 0.75$ but, in the middle part of the compositional range, become intermediate between those of the two sanidine series and the two more-ordered, topochemically monoclinic feldspar series.

It has been suggested that unit-cell volume is a good measure of composition in alkali feldspars because of its insensitivity to Al-Si distribution, particularly for strained feldspars (Smith, 1961) in which the a dimension is affected by the strain and is not useful for composition determination. Based on the two sanidine series, the appropriate equation for compositional determination in disordered feldspars is

$$N_{Or} = -238.102 + 1.09469V - (1.69255 \times 10^{-3})V^2 + (8.79388 \times 10^{-7})V^3. \quad (5)$$

Based on data for the orthoclase and adularia series, the equation for relatively ordered topochemically monoclinic feldspars is

$$N_{Or} = -129.248 + 0.610959V - (9.76800 \times 10^{-4})V^2 + (5.26832 \times 10^{-7})V^3. \quad (6)$$

And based on data for the microcline series reported here, plus the data of Orville (1967), the equation for topochemically triclinic series is

$$N_{Or} = -712.924 + 3.16601V - (4.70247 \times 10^{-3})V^2 + (2.33648 \times 10^{-6})V^3. \quad (7)$$

The three curves representing these equations are shown in Figure 8B (compare with Kroll and Ribbe, 1983, p. 72 and 74). These equations generally reproduced input compositions to within 0.02 in N_{Or} , or better.

A K/(K + Na) ratio given by any equation based on a or on volume will be in error if significant amounts of solid-solution impurities are incorporated into the feldspar in question. And for a strained feldspar, even Equations 5, 6, and 7 are certain to produce slightly erroneous results. Griffen and Johnson (1984) have shown that strain affects all the cell dimensions of an alkali feldspar, so it is certain to affect cell volume to at least a small degree. *There is no substitute for a direct chemical analysis*, even if it is a partial analysis for the major A-site cations.

X-ray data

One of the important results of a study such as the present one is a knowledge of how the individual X-ray peaks of alkali feldspars vary with composition, symmetry, and Al-Si order. Diagrams that are useful for indexing peaks on X-ray charts for feldspars like those studied in this investigation have been constructed and will be presented in a separate paper (Hovis, in prep.).

DETERMINATION OF THE STATE OF AL-SI ORDER IN ALKALI FELDSPARS

The b - c plot

Perhaps the most important use of unit-cell dimension data for alkali feldspars is for characterization of their chemical compositions and structural states, both in terms of symmetry and Al-Si distribution. Wright and Stewart (1968, p. 46) were the first to suggest that a plot of the b against the c unit-cell dimensions of an alkali feldspar would give a good estimate of both its K/(K + Na) ratio and its state of Al-Si order. Later, Stewart and Ribbe (1969) made formal use of the b - c plot to estimate the mole fraction of Al in T_1 and T_2 tetrahedral positions for both topochemically monoclinic and triclinic feldspars using the ordering parameter $\Delta(bc)$. Endmember unit-cell dimensions on which the $\Delta(bc)$ parameter was based have since been revised by Stewart and Wright (1974) and by

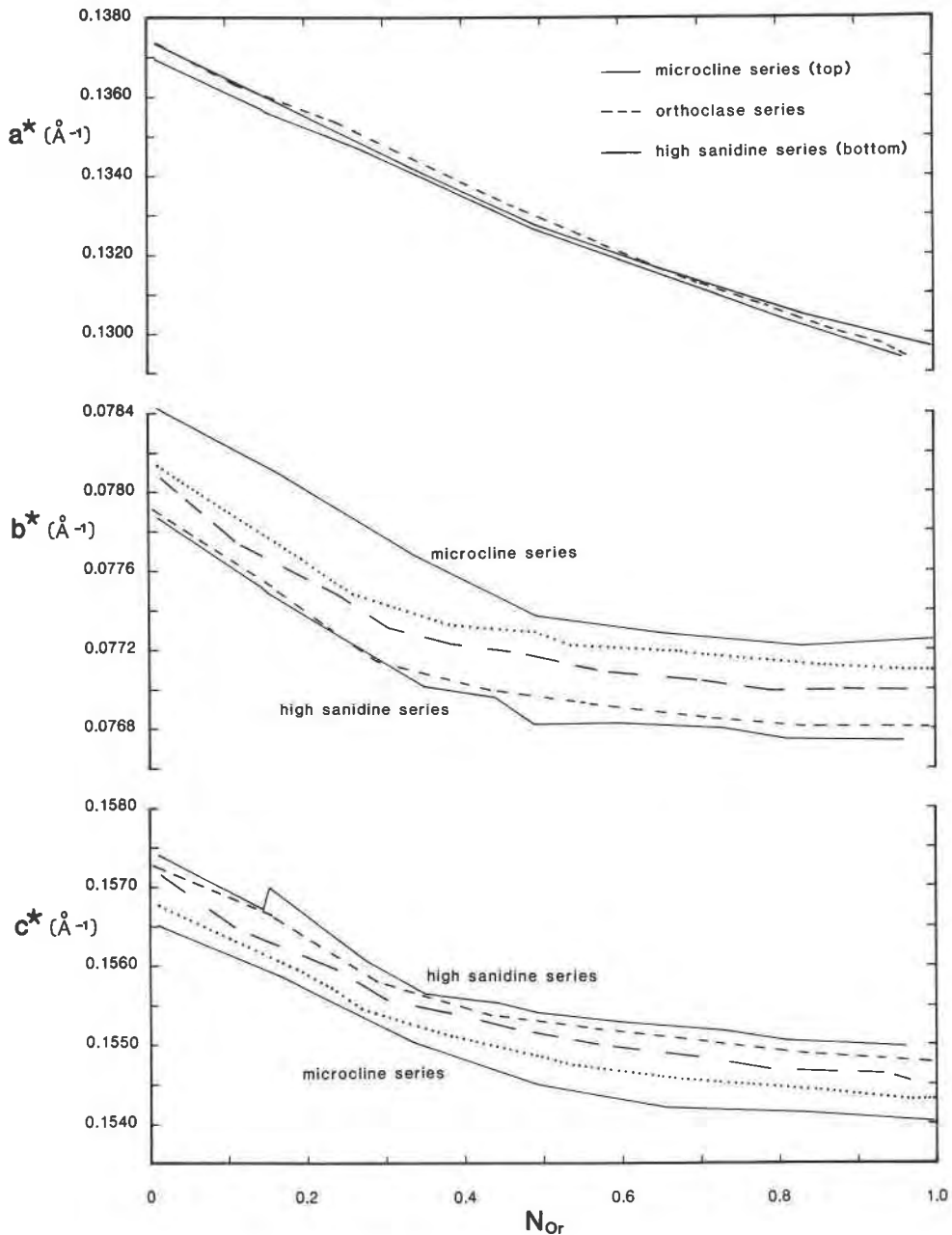


Fig. 6. Reciprocal unit-cell dimensions as functions of N_{Or} . Curves shown are not least-squares fits, but rather connect data points for individual series members. However, for clarity, the data points themselves are not shown. For a^* , because of the close spacing of the curves, data are shown only for the microcline series (top solid curve), the orthoclase series (dashes), and the high sanidine series (bottom solid curve). For b^* , the sequence from top to bottom is microcline (solid curve), adularia (dots), orthoclase (long dashes), Eifel sanidine (short dashes), and high sanidine (solid curve). Symbols for c^* are the same as for b^* , but note that the sequence is reversed with high sanidine on the top and microcline on the bottom.

Kroll and Ribbe (1983). The latter authors also have suggested that separate plots be used to estimate T_1 and T_2 contents for topochemically monoclinic vs. topochemically triclinic alkali feldspars. Furthermore, instead of using the $\Delta(bc)$ parameter to estimate Al-Si distributions, Kroll and Ribbe (1983) have given equations to estimate site occupancies directly from the b and c unit-cell di-

mensions of an alkali feldspar, a method originally suggested and used by Hovis (1974, Eqs. 3, 4a, and 4b).

Since the precise and accurate determination of Al-Si distributions in alkali feldspars can be of great importance, especially in the calculation of thermodynamic data, it is worthwhile to examine precisely how b and c behave as functions of one another. The following discussion will

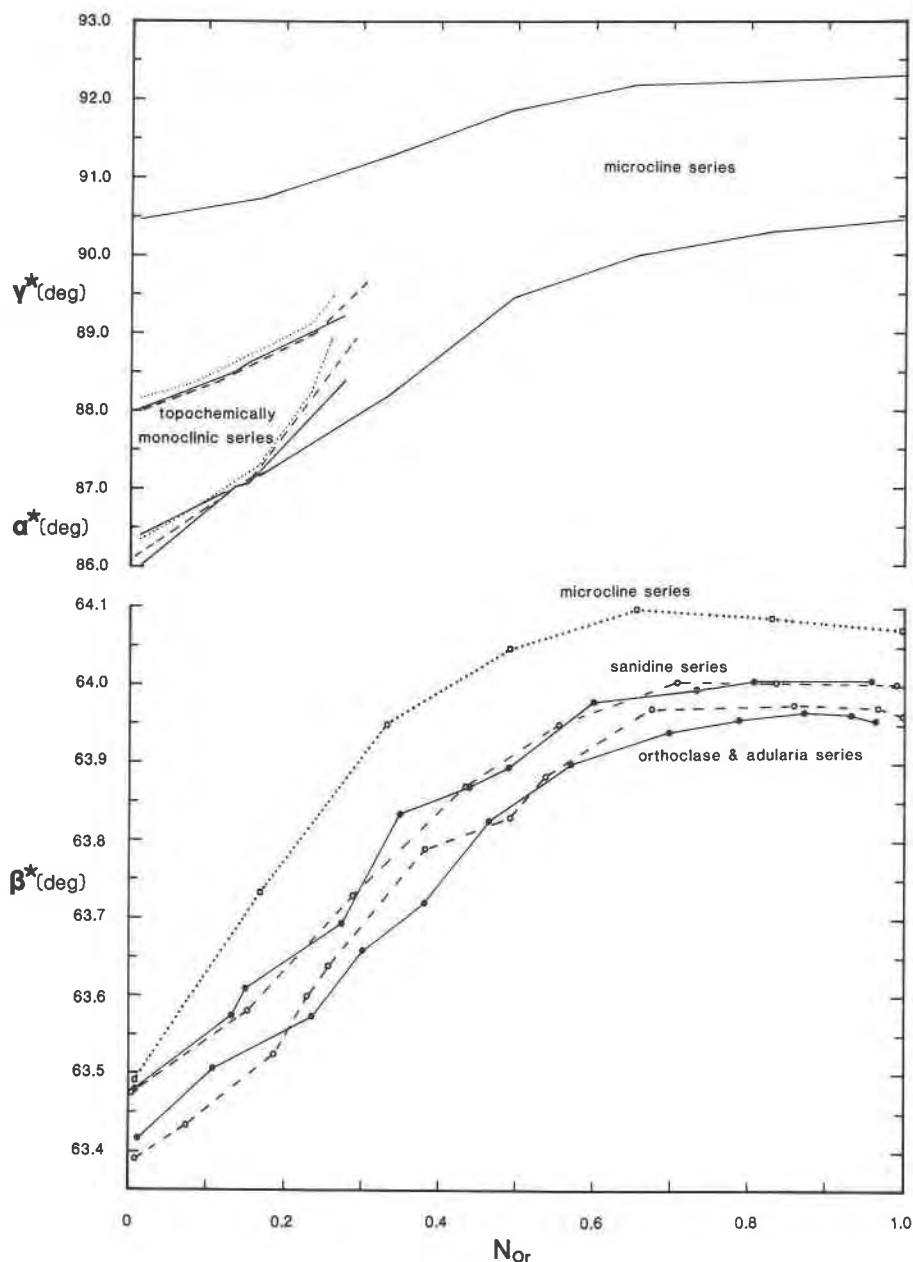


Fig. 7. Reciprocal unit-cell interaxial angles. Curves simply connect data points for individual series members. For α^* and γ^* , the continuous solid curve over the whole compositional range is for the microcline series. For clarity only three of the topochemically monoclinic series are shown, the adularia series (dotted), the orthoclase series (dashed), and the high sanidine series (solid). For β^* , all series are shown, microcline (open squares, dotted curve) at the top, high sanidine (solid curve) and Eifel sanidine (dashes) in the middle, and orthoclase (solid curve) and adularia (dashes) at the bottom.

necessarily dwell on the distribution of Al and Si between T_1 and T_2 tetrahedral sites, and not between “O” and “m” sites, since most of the new data are for topochemically monoclinic feldspars.

The main assumption made in the use of the b - c plot to estimate Al-Si distributions has been that b behaves as a linear function of c across all alkali feldspar ion-exchange series (see Figs. 4a and 4b of Kroll and Ribbe, 1983). An additional assumption made in using the $\Delta(bc)$ parameter

was that the $\Delta c/\Delta b$ slopes of the various series systematically decrease from microcline-low albite to sanidine-analbite series. In the more recent use of the b - c plot by Kroll and Ribbe (1983) this has changed; one slope is used for microcline series, while all topochemically monoclinic series are assumed to have a different, but constant, $\Delta c/\Delta b$ slope of 0.434. The new body of unit-cell data in Table 6 has allowed the testing of these assumptions.

Least-squares analyses of b - c data were performed for

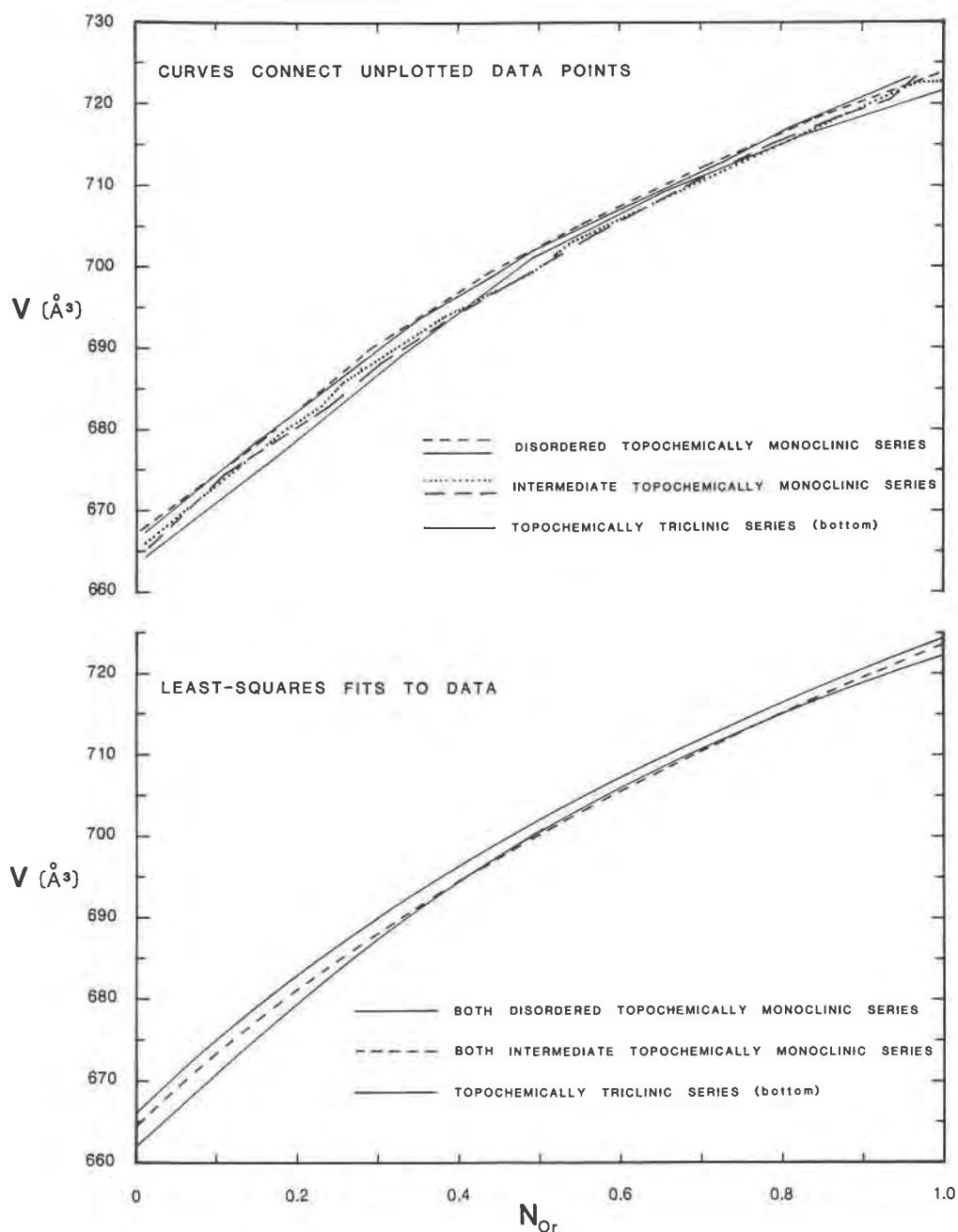


Fig. 8A (top). Unit-cell volumes as functions of N_{Or} . Curves shown connect data points for the high sanidine series (top solid curve), the Eifel sanidine series (short dashes), the orthoclase series (long dashes), the adularia series (dots), and the microcline series (bottom solid curve). Note the overlap between data for the two sanidine series, as well as for the orthoclase and adularia series, over most of the compositional range.

Fig. 8B (bottom). Unit-cell volumes as functions of N_{Or} . Curves represent least-squares fits to data for the sanidine series (top solid curve), the orthoclase and adularia series (dashes), and the microcline series of both this investigation and that of Orville (1967) (bottom solid curve) as expressed by Equations 5, 6, and 7.

entire feldspar series as well as for triclinic and monoclinic segments of topochemically monoclinic series (and sodic and potassic segments of the microcline series). There are several indications that b and c are not linear functions of one another over entire feldspar series (except possibly

for series that are extremely disordered). First, when best lines are fit for each series, the resulting distribution of data points about each line is systematic, with data points near endmember compositions falling above the lines and for intermediate compositions below the lines (Fig. 9),

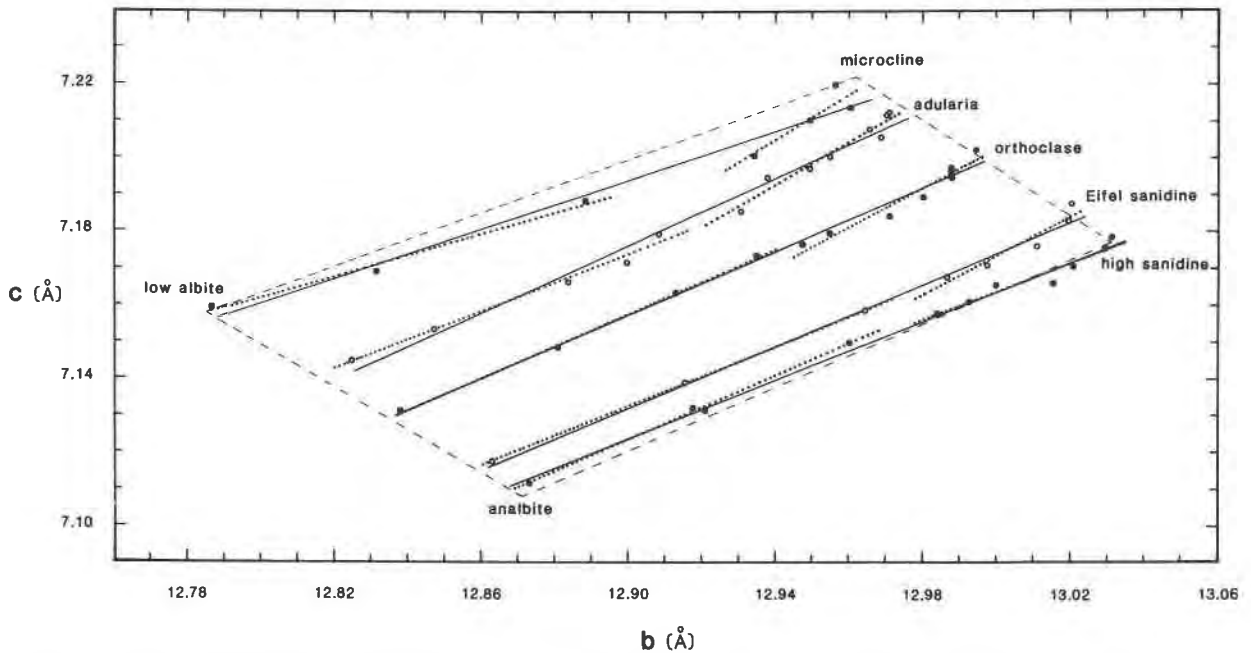


Fig. 9. Plot of the b and c unit-cell dimensions of all alkali feldspars of this investigation. Solid lines represent linear least-squares fits of b as a function of c for all members of each series. Dotted lines represent separate least-squares fits for triclinic vs. monoclinic segments of topochemically monoclinic series, or for sodic vs. potassic segments of the microcline series. Light dashes connect b - c values for alkali feldspar endmembers as suggested by Kroll and Ribbe (1983).

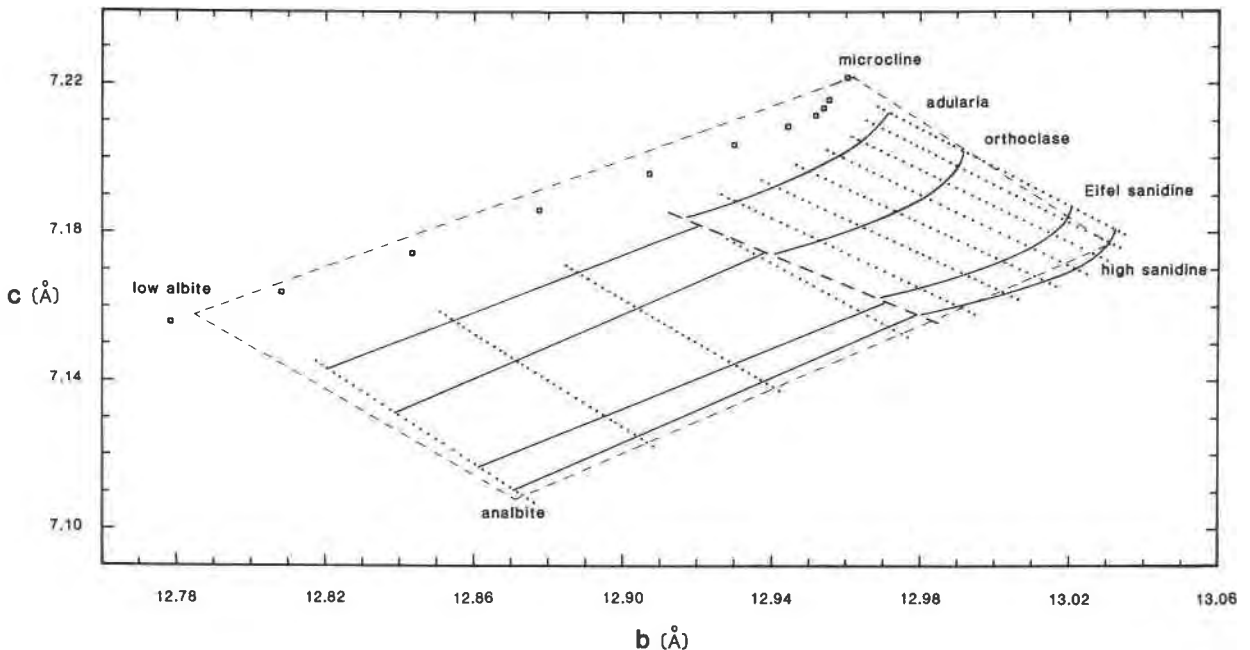


Fig. 10. Plot of b - c relations for alkali feldspars of the present investigation. Behavior in topochemically monoclinic series is shown by the solid curves, which represent changes in b - c values along each ion-exchange series, determined by solving equations in Table 9 as a function of N_{Or} . The heavy dashed line represents the position of the triclinic-monoclinic displacive transformation at room temperature and pressure. Dotted lines are isochemical and drawn at intervals of 0.1 from an N_{Or} of 0.0 at the left to 1.0 at the right. For microcline series, open squares represent solutions to fourth-order equations for b and c for the combined data of the present investigation and those of Orville (1967), also at intervals of 0.1 in N_{Or} . The spacing of points at the K-rich end of the microcline series is due to the leveling off of b with composition. Light dashed lines on this diagram connect b - c values suggested by Kroll and Ribbe (1983) for alkali feldspar end members.

Table 11. Successive linear least-squares fits of c as a function of b starting from sodic and potassic ends of the feldspar series of this investigation

Series	Number of data points	From sodic ends of series		From potassic ends of series		
		Standard deviation of fit (Å)	Slope	Standard deviation of fit (Å)	Slope	
High sanidine	3	.0016	.430	.0014	.710	
	4	.0012	.437	.0010	.726	
	5	.0013	.419	.0029	.404	
	6	.0013	.412	.0025	.392	
	7	.0012	.415	.0022	.386	
	8	.0021	.397	.0021	.369	
	9	.0020	.393	.0021	.393	
	10	.0019	.394	.0020	.390	
	11	.0019	.399	.0019	.399	
	Eifel sanidine	3	.0002	.406	.0027	1.077
		4	.0002	.407	.0030	.658
5		.0005	.402	.0030	.533	
6		.0007	.398	.0028	.471	
7		.0012	.406	.0027	.430	
8		.0025	.420	.0025	.420	
Orthoclase		3	.0010	.423	.0007	.839
		4	.0009	.434	.0012	.929
	5	.0013	.420	.0010	.986	
	6	.0012	.415	.0012	.765	
	7	.0014	.405	.0022	.571	
	8	.0013	.403	.0022	.527	
	9	.0014	.409	.0025	.469	
	10	.0016	.416	.0025	.445	
	11	.0018	.422	.0023	.440	
	12	.0023	.431	.0023	.431	
	Adularia	3*	.0004	.361	-	-
		4	.0003	.356	.0028	.931
5		.0018	.385	.0024	.666	
6		.0015	.385	.0021	.645	
7		.0027	.414	.0024	.522	
8		.0025	.420	.0024	.573	
9		.0024	.426	.0025	.519	
10*		-	-	.0024	.525	
11		.0024	.437	.0023	.511	
12		.0027	.447	.0027	.475	
13		.0029	.455	.0029	.455	
Microcline		3	.0022	.288	.0062	.397
		4	.0016	.287	.0046	.616
	5	.0025	.307	.0046	.395	
	6	.0024	.314	.0041	.362	
	7	.0042	.332	.0042	.332	

*Members of #7007 and 7198 of the adularia series have identical compositions, thus the absence of a 3-point fit from the potassium end and a 10-point fit from the sodium end of that series.

indicating a concave-up b - c relationship in the general case. This is due mainly to the tendency of b to level off with increasing K content while c continues to increase. Even if b were a linear function of c , the $\Delta c/\Delta b$ slopes would not be constant, varying from 0.40 for the sanidine series to 0.46 for the adularia series (Fig. 9). Second, when lines are fit separately to triclinic and monoclinic segments of each series, the differences in the two slopes systematically decrease from adularia to orthoclase to sanidine, to the point where they are virtually identical in the most disordered series (Fig. 9). (If potassic and sodic segments of the microcline series are fit separately, the difference in slope is even greater than in adularia, suggesting that this pattern extends to triclinic series.) Finally, when linear least-squares fits are performed on successively larger groups of data points starting from either the Na-rich or the K-rich end of each series, slopes systematically change (Table 11). The effect is particularly dramatic when starting from the potassic end of a series where initial slopes of 0.6 to 1.0 (as opposed to the generalized slopes of 0.4 that are currently used for entire series) rapidly decrease

Table 12. Equations for isochemical lines for topochemically monoclinic feldspars on a plot of c vs. b

Composition, N_{Or}	Least-squares coefficients	
	a_0	a_1
0.0	15.552	-.6559
0.1	15.164	-.6229
0.2	14.672	-.5822
0.3	14.204	-.5434
0.4	13.258	-.4694
0.5	13.236	-.4670
0.6	13.260	-.4682
0.7	13.351	-.4746
0.8	13.487	-.4846
0.9	13.694	-.5000
1.0	13.998	-.5231

Equations have the form:
 c (Å) = $a_0 + a_1 b$

as more data are added. The changes are not as dramatic starting from the sodic ends of the series, pointing to the disproportionate influence of sodic members on $\Delta c/\Delta b$ slopes. In fact, it is the large changes of both b and c with composition at sodic compositions that control the $\Delta c/\Delta b$ slopes, yet it is mainly for the characterization of natural potassic feldspars that the b - c plot is useful.

When triclinic and monoclinic segments of topochemically monoclinic series are treated separately, it is only in the triclinic segment of each series that b and c are linear functions of each other, a fact not surprising in that individually these parameters behave linearly with composition in this region. In monoclinic segments of series, at least quadratic fits to b - c data are required, since for linear fits, data near the endmembers fall above and data in between fall below the lines (Fig. 9). This too is not unexpected in view of the nonlinear behavior of b but the linear behavior of c in the monoclinic compositional range.

Although nonlinear b - c relationships are clearly required, simple quadratic fits of c as a function of b do not represent the data well, since the curvature in each series is not spread evenly across the monoclinic compositional range, but occurs rather abruptly at N_{Or} values above approximately 0.75. The most satisfactory representation of c as a function of b was found by employing the relationships for each of these parameters (Table 9) in terms of N_{Or} to determine b - c pairs at specific values of N_{Or} . It was in this way that the curves in Figure 10, representing b - c behavior for the various ion-exchange series reported in this paper, were determined. It also was this method that allowed the calculation of isochemical lines on the b - c quadrilateral. For each of the four topochemically monoclinic series, b - c pairs were determined for particular values of N_{Or} . The four points at each composition then were linearly fit by least-squares to obtain the isochemical lines shown. Equations for these lines are given in Table 12. Note that these are based on an internally consistent set of chemical data (Table 3).

Several features of the b - c plot of Figure 10 are worth noting. First, in addition to the fact that c is not a linear function of b , neither are the various series perfectly parallel to each other. Second, isochemical lines for topochemically monoclinic series at N_{Or} values of 0.0 and 1.0

Table 13. Data used to determine the Z - c_K relationships of Figure 11 and Equations 13, 14, and 15

Monoclinic feldspar	Reference(s)	N_{An} ($=\frac{N_{An}}{N_{Or}+N_{Ab}+N_{An}}$)	N_{Or} ($=\frac{N_{Or}}{N_{Or}+N_{Ab}}$)	Grand mean T-0 distance	Mean T-0 distances (\AA)		c_{obs} (\AA)	Calculated Z	Calculated Y	Calculated c_K (\AA)		
					T_1	T_2						
Annealed Eifel Sanidine	1	0.0002	0.888	1.64275	1.64500	1.64050	7.178	0.072	0	7.1823		
Annealed Spencer C	2,3	0.0050	0.9179	1.64213	1.64450	1.63975	7.1749	0.076	0	7.1780		
Eifel Sanidine 70Q2	4	0.0005	0.8542	1.64313	1.64925	1.63700	7.179	0.196	0	7.1845		
Eifel Sanidine 70Q2	5	0.0002**	0.8359**	1.64225	1.64975	1.63475	7.179	0.240	0	7.1852		
Eifel Sanidine 70Q2	6	0.0002**	0.8359**	1.64138	1.65100	1.63175	7.183	0.308	0	7.1892		
Eifel Sanidine 70Q2	7	0.0002	0.8359	-	-	-	-	0.248*	0	7.1879*		
Eifel Sanidine (not 70Q2)	1	0.0002	0.900	1.64375	1.64250	1.63500	7.188	0.280	0	7.1918		
Spencer C	8	0.0050	0.9179	1.64188	1.65550	1.62825	7.1934	0.436	0	7.1965		
Spencer B	8	0.0005	0.9003	1.64275	1.66350	1.62200	7.207	0.664	0	7.2108		
Adularia 7007	4	0.0020	0.8808	1.64325	1.66525	1.65125	7.201	0.704	0	7.2055		
Adularia 7007	7	0.0009	0.8602	-	-	-	-	0.704*	0	7.2128*		
Himalayan Orthoclase	9	0.0025	0.8933	1.64188	1.66750	1.61625	7.2099	0.820	0	7.2140, 7.2137		
			0.8999 [†]									
Triclinic feldspar					T_1^0	T_1^m	T_2^0	T_2^m				
P2B	10,11	0.009	0.944	1.64425	1.65950	1.65700	1.63075	1.62975	7.197	0.448	0.020	7.1991
P2A	10,11	0.009	0.944	1.64306	1.66500	1.65550	1.62550	1.62625	7.202	0.550	0.076	7.2041
P17C	10,11	0.001	0.880	1.64188	1.66900	1.65375	1.62300	1.62175	7.200	0.624	0.122	7.2046
A1D	10,11	0.005	0.914	1.64225	1.67350	1.65075	1.62350	1.62125	7.201	0.636	0.182	7.2043
CA1A	10,11	0.003	0.899	1.64406	1.67225	1.65875	1.62275	1.62250	7.210	0.686	0.108	7.2128*
P1C	10,11	0.005	0.911	1.64250	1.70075	1.63050	1.61975	1.61900	7.210	0.740	0.562	7.2134
CA1B	10,11	0.003	0.899	1.64381	1.69425	1.64275	1.61950	1.61875	7.209	0.790	0.412	7.2128
Spencer U	12,13 ^{††}	0.014	0.937	1.64281	1.69425	1.64250	1.61850	1.61600	7.213	0.818	0.414	7.2154
RC20C	10,11	0.009	0.865	1.64431	1.71700	1.62950	1.61525	1.61550	7.221	0.926	0.700	7.2261
CA1E	10,11	0.003	0.899	1.64544	1.73125	1.61800	1.61625	1.61625	7.223	0.934	0.906	7.2238
Pontiskalk	14	0	0.948	1.64406	1.73475	1.61325	1.61900	1.60925	7.2188	0.958	0.972	7.2208
Microcline Prilep	15	0	0.965	1.64500	1.738	1.613	1.614	1.615	7.2211	0.976	1.000	7.2224
Microcline												

References:

- Weitz, 1972
- Cole et al., 1949
- Ribbe, 1963
- Phillips and Ribbe, 1973
- Brown et al., 1977
- Ohashi and Finger, 1974
- Hovis, 1974 and this investigation
- Colville and Ribbe, 1968
- Prince et al., 1973
- Dal Negro et al., 1978
- Dal Negro et al., 1980
- Bailey, 1969
- Wright and Stewart, 1968
- Finney and Bailey, 1964
- Strob (1983), as reported in Kroll and Ribbe, 1983

*Z for Eifel Sanidine is an average value based on references #4, 5, and 6; for adularia it is that of reference #4. c_K values are based on c -values for all monoclinic members of the two ion-exchange series.

**Chemical data of the present investigation and c -values of the investigators listed were used to determine c_K .

[†]First value from wet chemical analysis, second from electron microprobe.

^{††}Chemical and cell dimension data from reference #13, and distances from reference #12.

do not coincide with any of the previously proposed sides for the alkali feldspar quadrilateral (Wright and Stewart, 1968; Stewart and Wright, 1974; Kroll and Ribbe, 1983). The line representing pure-K feldspars has a shallower slope and that representing pure-Na analbites a steeper slope than those which have been previously suggested. Furthermore, the slopes of the isochemical lines systematically change as they sweep across the diagram.

Although the b - c plot remains an excellent means for determining approximate compositions and T_1 - T_2 site populations in alkali feldspars, a more precise method is needed for quantitative determination of Al-Si distribution.

A new ordering parameter, c_K

The c unit-cell dimension not only behaves linearly with composition in both triclinic and monoclinic parts of topochemically monoclinic alkali feldspar series, but slopes for all series are virtually identical, averaging $0.038 \pm 0.003 \text{ \AA}$ in the monoclinic compositional range and

$0.140 \pm 0.007 \text{ \AA}$ in the triclinic range (Fig. 3, Table 9). Linearity with composition even extends to the potassic region of microcline series. Thus, at any one composition, the observed c value of an alkali feldspar is unique and a measure of its Al-Si distribution. If the c values of a group of alkali feldspars having various compositions and Al-Si distributions were corrected to a common composition, the feldspars could easily be ranked from most ordered (highest corrected c value) to least ordered (lowest corrected c value).

Although the correction of observed c values of alkali feldspars (c_{obs}) to any composition would work equally well, let us correct these values to those of pure-K end-members (thus the designation of this parameter as c_K) since it is mostly for natural potassic feldspars that Al-Si distributions are calculated. For any monoclinic feldspar, or for a microcline series member with an N_{Or} value between 0.4 and 1.0, the equation that makes this correction is

$$c_K = c_{obs} + 0.038(1 - N_{Or}). \quad (8)$$

For a triclinic feldspar in a topochemically monoclinic feldspar series, the pertinent equation is

$$c_K = c_{\text{obs}} - 0.140N_{\text{Or}} + 0.0706. \quad (9)$$

For microcline series members with N_{Or} values between 0.0 and 0.4, c_K is calculated according to the nonlinear relationship

$$c_K = c_{\text{obs}} + 0.0658079 - 0.0574870N_{\text{Or}} - 0.280817N_{\text{Or}}^2 + 0.554786N_{\text{Or}}^3 - 0.282289N_{\text{Or}}^4. \quad (10)$$

In calculating c_K , one is essentially sliding the observed c value of an alkali feldspar along the c - N_{Or} lines of Figure 3 to the K end of an ion-exchange series, thereby subtracting the effect of composition on c and allowing its value to be determined entirely by Al-Si distribution.

Values of c_K calculated for feldspars in the literature range from approximately 7.180 Å for the most disordered to about 7.214 Å for the most ordered monoclinic feldspar (specifically the ordered "orthoclase" investigated by Prince et al., 1973). Maximum microclines have an average c_K value of about 7.222 Å (Table 13).

The high precision with which the c unit-cell dimension can be determined (generally to within 0.001 Å) considered against the 0.042-Å difference in c_K values for the most ordered versus the most disordered alkali feldspars makes evident the usefulness of c_K as an effective parameter for characterizing the relative Al-Si distribution of an alkali feldspar. For thermodynamic and other calculations, however, we wish to go one step farther and calculate the actual Al-Si distribution of the feldspar.

Correlation of c_K with Al-Si distribution

In the past, Al-Si distributions of alkali feldspars have generally been determined from the tetrahedral bond-length data of single-crystal studies. It seemed feasible to correlate these distributions with calculated c_K values for the feldspars that have been investigated. To date, ten single-crystal studies have been conducted on K-rich monoclinic alkali feldspars. These are listed in Table 2 of Kroll and Ribbe (1983). In attempting to use these data, however, several problems were encountered. First, most of the N_{Or} values given in the Kroll and Ribbe table were in error compared with values given in the original publications from which the data came. Second, round-off errors were found in four of the average T-O distances stated in the table. Third, it should have been noted in the table that three of the Eifel sanidine structural analyses [those by Phillips and Ribbe (1973), Brown et al. (1974), and Ohashi and Finger (1975)] were done on chips of material originating from the same feldspar specimen, given to other laboratories by the late D. R. Waldbaum: all of these should be labeled as no. 7002. The data of these workers may validly be compared. The analyses by Weitz (1972) on Eifel sanidine and its heated equivalent, however, were performed on a different specimen. Lastly, Table 2 of Kroll and Ribbe (1983) failed to indicate that chemical analytical and unit-cell data in addition to those given by Phillips and Ribbe (1973) exist on adularia no.

7007 and Eifel sanidine no. 7002 (Hovis, 1974; also, additional data in this paper).

Because of these problems the Al-Si distributions based on the ten studies listed in Table 2 of Kroll and Ribbe (1983) were reformulated (using Eq. 5 of the same authors). These distributions are presented in Table 13 and are expressed in terms of Z (Thompson, 1969, 1970) as

$$Z \equiv N_{\text{Al(T1O)}} + N_{\text{Al(T1m)}} - N_{\text{Al(T2O)}} - N_{\text{Al(T2m)}} \quad (11)$$

for topochemically triclinic feldspars, which reduces to

$$Z \equiv 2[N_{\text{Al(T1)}} - N_{\text{Al(T2)}}] \quad (12)$$

for topochemically monoclinic feldspars (owing to the equivalency of "O" and "m" tetrahedral sites in such feldspars). Average T-O distances reported in Table 13 are given with a large number of significant figures, clearly beyond the precision of the original data, in order to avoid round-off error in calculating values of Z . Note that the latter values are given with fewer significant figures.

Table 13 also includes c_K values for the feldspars based on the correct N_{Or} (and c_{obs}) values taken directly from the original references. The stated N_{Or} values only take into account Na and K for all feldspars and ignore other solid-solution substitutions. In addition, extra c_K values for adularia no. 7007 and Eifel sanidine no. 7002 are given, based on my own data. These are from linear fits of c as a function of N_{Or} for the monoclinic parts of these two ion-exchange series (equations in Table 9) and are not those calculated simply from the c_{obs} and N_{Or} values of the natural parent materials, though there would be insignificant differences if the latter values had been used instead (7.2127 vs. 7.2128 Å for adularia, and 7.1879 vs. 7.1891 Å for Eifel sanidine). The Z value correlated with the c_K for adularia is based on the data of Phillips and Ribbe (1973), whereas the Z value used for the Eifel sanidine is an average based on the three single-crystal studies done on specimen no. 7002.

A least-squares analysis of the data for the topochemically monoclinic alkali feldspars listed in Table 13 indicated that a linear fit to the data was best:

$$Z = -144.962 + 20.2032c_K. \quad (13)$$

The twelve data points for these feldspars are plotted on Figure 11, and the relationship indicated by Equation 13 is shown as the upper dashed line on the diagram.

It was a natural extension of this work to try a similar analysis for topochemically triclinic feldspars. Though these feldspars undergo no triclinic-monoclinic inversion, behavior of the c unit-cell dimension with composition was noted earlier in this paper to be very similar to that of topochemically monoclinic series, especially for feldspars with N_{Or} values above approximately 0.4. On the basis of the low albite-microcline series reported in this paper, as well as that of Orville (1967), c_K for potassic members of such series can also be computed using Equation 8.

All potassic topochemically triclinic alkali feldspars for which single-crystal data are available have been listed in

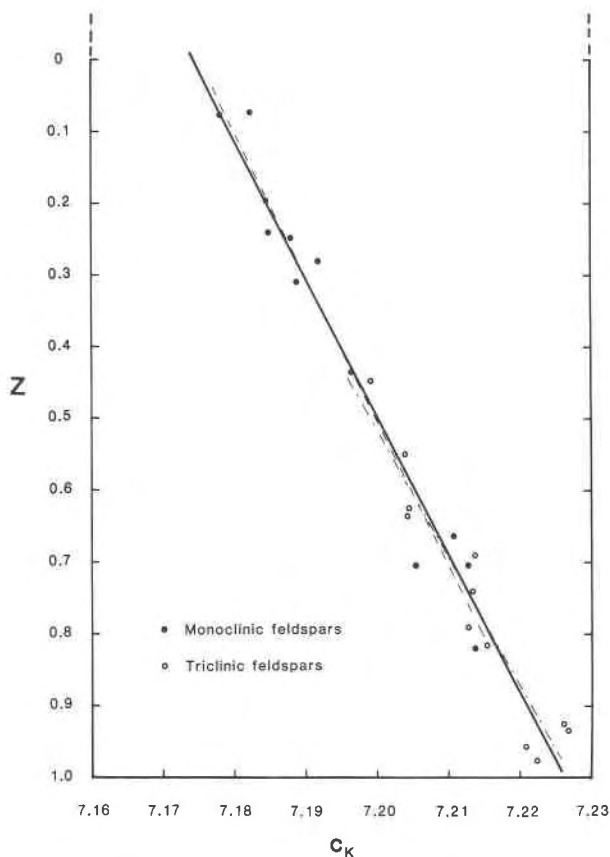


Fig. 11. Plot of Z (for definition, see Eqs. 11 and 12) against c_K . Solid circles represent data for monoclinic feldspars, and open circles are for triclinic feldspars (see Table 13). Heavy solid line is the linear least-squares fit to all data (Eq. 15), the upper dashed line is the fit to monoclinic data only (Eq. 13), and the lower dash-dot line is the fit to triclinic data only (Eq. 14). Note the very close proximity of the latter two lines to the fit for all data. Upward extension of the diagram emphasizes that ordering between the T_1 and T_2 sites in alkali feldspars is nonconvergent (Thompson, 1969 and 1970).

Table 13 (also see Table 3 in Kroll and Ribbe, 1983). Note that Z values calculated for these feldspars are defined by Equation 11. Original sources were checked for N_{Or} values; only the unpublished data of Strob (1983) were taken directly from Table 3 of Kroll and Ribbe (1983). Corrected unit-cell dimension data (for c_{obs}) as given by Dal Negro et al. (1980) were used for the intermediate microclines reported previously (1978) by those authors. Again, the average T-O distances given are stated to a larger number of significant figures than can be justified in order to avoid round-off error in the calculation of the ordering parameters Z and Y [$\equiv N_{Al(T1O)} - N_{Al(T1m)}$].

As with monoclinic feldspars, a linear regression was found to be best for topochemically triclinic feldspars:

$$Z = -128.270 + 17.8866c_K. \quad (14)$$

Two of the data points included in Table 3 of Kroll and Ribbe (1983) were not used in the regression—interme-

diate microcline K235 because it was a strained feldspar and plotted away from the other data and Pellotsalo microcline (Brown and Bailey, 1964) because data from the latter publication gave a very large and physically unattainable value of Z (1.07). The data points for topochemically triclinic feldspars are shown as open symbols in Figure 11, and the relationship given by Equation 14 is shown as a dot-dash line toward the bottom of the diagram. Note the near-coincidence of this line with the dashed line representing relations for monoclinic feldspars, even though the two are based on entirely different sets of data. Furthermore, feldspars with vastly different values of Y (see Table 13) plot near the calculated line and are scattered only slightly more than monoclinic data points of the same figure. Thus, Z - c_K relations are affected substantially neither by the displacive transformation nor by Y ordering. It appeared, then, that a single equation could be employed to determine T_1 - T_2 site occupancies for all alkali feldspars. Least-squares analysis of data for both monoclinic and triclinic feldspars resulted in the following relationship:

$$Z = -138.575 + 19.3153c_K, \quad (15)$$

which is represented by the prominent solid line on Figure 11. On the basis of Equation 15, one can calculate fractions of Al and Si in the T_1 and T_2 tetrahedral sites as follows:

$$N_{Al(T1)} = (1 + Z)/4 \quad (16)$$

$$= -34.3939 + 4.82884c_K. \quad (17)$$

$$N_{Al(T2)} = (1 - Z)/4 \quad (18)$$

$$= 34.8939 - 4.82884c_K. \quad (19)$$

$$N_{Si(T1)} = 1 - N_{Al(T1)} = (3 - Z)/4 \quad (20)$$

$$= 35.3939 - 4.82884c_K. \quad (21)$$

$$N_{Si(T2)} = 1 - N_{Al(T2)} = (3 + Z)/4 \quad (22)$$

$$= -33.8939 + 4.82884c_K. \quad (23)$$

Values of Z have been calculated for all feldspars of the present investigation. The standard deviation in Z for all series is about 0.03. Since Z is twice the difference in the mole fractions of Al in the T_1 and T_2 sites, an uncertainty of 0.03 in Z correlates with an uncertainty of ± 0.008 for the mole fraction of Al in either of the tetrahedral sites. Thus, for most alkali feldspars, use of Equation 15 will result in knowing the amount of Al in the T_1 and T_2 tetrahedral sites to within less than 1 mol% Al of those amounts that would have been derived from a direct single-crystal analysis on the specimen. (For topochemically triclinic feldspars, note that additional characterization is needed to determine "O" versus "m" site occupancies.)

Accuracy versus precision

Since most of the single-crystal data in Table 13 come from X-ray diffraction studies, Al-Si distributions calculated from Equation 15 will be more consistent with those determined from X-ray data than with those based on other experimental techniques. As an example, one can compare a Z value of 0.907 for Amelia low albite—based on the bond lengths derived from the single-crystal X-ray

diffraction data of Harlow and Brown (1980) and on Equation 5 of Kroll and Ribbe (1983) with a "const" of 0.13, since Amelia low albite is a sodic feldspar—to the value of 0.883 determined from the c_K value (7.2202 Å) of the present Amelia-based microcline series. The two values are well within the uncertainties of each other but appear to disagree slightly with Z values based on bond lengths from neutron diffraction data ($Z = 0.940$; data of Harlow and Brown, 1980) or on the refinement of scattering lengths from neutron diffraction data ($Z = 1.004$; Smith et al., 1986, and pers. comm.), the latter indicating Amelia low albite to be fully ordered (within experimental error). Z values of 1.0 and 0.9 correspond to having no Al in either of the T_2 sites versus having 2.5% Al in each. Thus, this difference is not as large as might first appear. Nevertheless, it must be recognized that different determinative techniques are not perfectly consistent with each other. Therefore, although the ordering parameter c_K should provide a more precise method than is currently used to determine Al-Si distributions between T_1 and T_2 sites in alkali feldspars, the accuracy of such determinations can come only when we are more confident that the various physical parameters of alkali feldspars, such as bond lengths and unit-cell dimensions, are being correlated with the correct site occupancies.

Estimation of Al-Si distribution directly from X-ray data

In addition to correlation with unit-cell dimensions, methods have been developed during the present study for the determination of Al-Si distribution in alkali feldspars directly from X-ray data. These will be presented in a future paper (Hovis, in prep.).

CONCLUDING COMMENTS

Unit-cell dimensions determined during the present investigation fill data gaps that previously existed for alkali feldspar ion-exchange series having relatively ordered topochemically monoclinic Al-Si distributions (like that of adularia no. 7007) and for sanidine series that are not fully disordered (like parent material no. 7002). Furthermore, three of the five ion-exchange series reported in this paper are based on parent materials on which extensive single-crystal work has previously been done and therefore on which Al-Si distributions are well characterized. In addition to the structural control on the series, comparisons of the variation of unit-cell dimensions from series to series have been based on an internally consistent set of chemical analyses for all feldspars.

One of the most important results of this work has been the conclusion that the c unit-cell dimension behaves linearly with composition in both the triclinic and monoclinic parts of all topochemically monoclinic series, as well as in the potassic part of microcline series. The constancy of the $\Delta c/\Delta N_{or}$ slopes has allowed the use of these relationships to develop a new ordering parameter c_K , which in turn has been used to give highly precise estimates of

the distribution of Al and Si between T_1 and T_2 sites in alkali feldspars. The increased precision with which these distributions can now be determined should be helpful in the calculation of thermodynamic data, phase equilibria, and other applications in which the maximum precision is required.

Data presented in this paper will provide the basis in future papers for analyses of volume changes with composition and ordering, the effect of Al-Si distribution on volumes of K-Na mixing, and the usefulness of individual diffraction maxima to characterize Al-Si distribution.

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